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The Photochemistry Of Adamantanethione

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THE PHOTOCHEMISTRY OF ADAMANTANETHIONE

by

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ABSTRACT

The rate constant for decay of adamantanethione triplet has been directly determined by laser flash photolysis and was found to be dependent on adamantanethione concentration, providing unequivocal evidence for direct interaction of adamantanethione triplets and ground state molecules.

The photodimerization and photocycloaddition of adamantanethione to ethyl vinyl ether at 500 nm have been studied kinetically. Evidence is provided that both reactions occur through the lowest triplet state of adamantanethione. The lifetime of the S_1 state, the triplet yield and the rate constant for intersystem crossing of adamantanethione have been estimated.

The photochemistry of adamantanethione at 250 nm has also been investigated. Dimerization is proposed to occur partially via direct excitation of ground state aggregates. When adamantanethione was irradiated in the presence of ethyl vinyl ether, two thietanes were obtained. This is the first example of non-regiospecificity observed in thioketone photochemistry. The complex mixture obtained upon irradiation of adamantanethione at short wavelength contains products originating from the interaction of the thione with the solvent. In cyclohexane for example, 2-cyclohexylthioadamantane and the corresponding thiol were isolated.

The Photoreduction of Adamantanethione with 2-adamantylthiol ($\lambda > 420$ nm) gives 2-adamantyldisulfide as the sole product. Evidence is provided that the mechanism involves a chain reaction.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

1.1 Photochemistry of Carbonyl Compounds

One of the most studied functional groups in organic photochemistry is the carbonyl group and, in particular, extensive work has been carried out on aromatic ketones. A complete description of ketone photochemistry is far beyond the purpose of this section and we shall only consider some cases which have been subjected to mechanistic scrutiny.

Benzophenone itself, the most highly studied aromatic ketone undergoes two important photochemical reactions. Firstly it undergoes photoreduction in hydrogen donor solvents to give benzpinacol 1 (1,2) and secondly it undergoes a photocycloaddition with olefins to give oxetanes (3).

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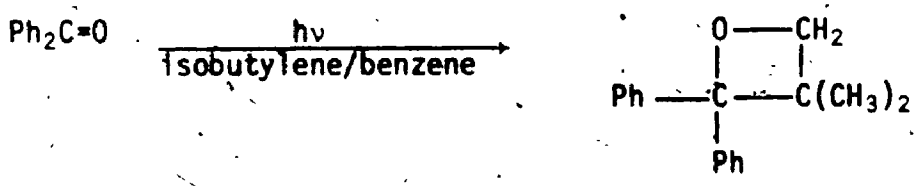


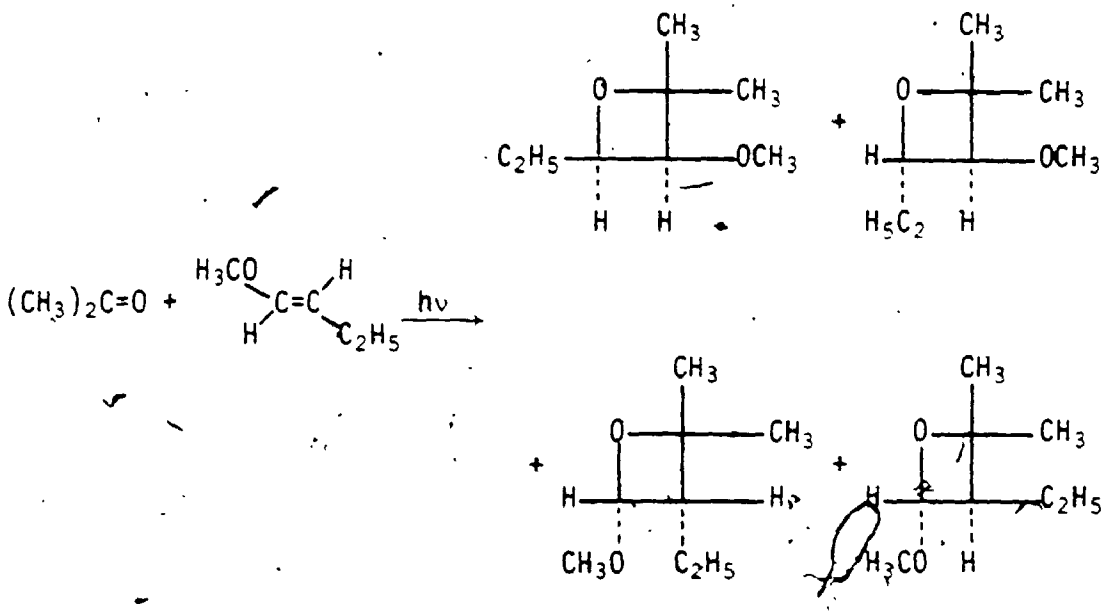
The photoreduction of benzophenone to benzpinacol in alcoholic solutions serves as a basis for the interpretation of the

photoreactions of aromatic ketones.

Hammond and coworkers (4,5) have demonstrated that the photoreduction of aromatic ketones proceeds through the n,π* triplet state. Upon irradiation, in alcoholic solvents, benzophenone which has a lowest n,π* triplet, is readily photoreduced; whereas 2-acetonaphthone, which has a lowest π,π* triplet, is not efficiently photoreduced. Photoreduction of 2-acetonaphthone can be achieved using tri-n-butylstannane (4), a far better hydrogen donor or triethylamine (6). However, the evidence for the n,π* triplet being the only reactive species for oxetane formation is not conclusive in all cases (7).

These results have led to the broad generalization, which inevitably has some exceptions, that aromatic ketones having as their lowest state a n,π* triplet will readily undergo photoreduction in hydrogen donor solvents and form oxetanes with simple olefins.

While singlet reactions are precluded with aromatic ketones due to the rapid rate of intersystem crossing of the latters (8), alkyl ketones have relatively long-lived S_1 states (relative to aryl ketones) and detailed kinetic analysis of the photocycloaddition of acetone to trans-1-methoxy-1-butene for example revealed that both acetone singlet and triplet state are involved in oxetane formation and that the reactivity of the two states are nearly equal (9).



The reactivity of n,π* triplet states of alkyl ketones in intermolecular hydrogen abstractions is not disputed but the extent of singlet participation is still unknown and further work must be done in this area (10).

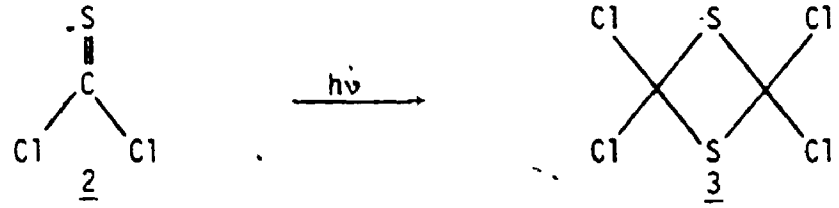
The relationship between the multiplicity as well as the electronic configuration of the low-lying excited states and the photochemical reactivity of ketones is not the only question that has occupied photochemists in the past decade. Considerable effort has been made toward the answering of many other questions relevant to the complete understanding of a photochemical reaction, the most important are; are there any intermediates involved in the process "Excited state → Product" and what is the nature of these intermediates? How did excited states which did not react return to ground state? In this respect, a variety of species (biradicals, excimers, exciplexes) have been proposed as reactive intermediates in ketone photochemistry based on direct observation or kinetic analysis.

Similarly, many energy-wasting processes have been elucitated in ketone photochemistry and these will be a matter of discussion in the following chapters.

1.2 Photochemistry of Thiocarbonyl Compounds

(a) Historical

Interest in the photochemistry of thiocarbonyl compounds began in 1933 when Schonberg and Stephenson (11) studied the photodimerization of thiophosgene 2.



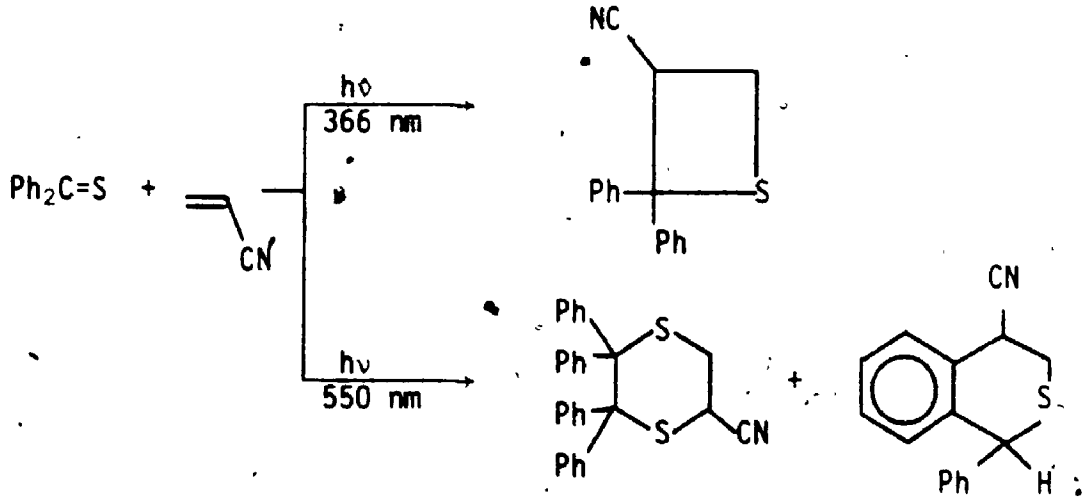
2 3

In 1943 Schonberg and Mostafa (12) investigated the photooxidation of several substituted thiobenzophenones, xanthiones and thioxanthiones. They found that thiobenzophenone decomposed in the presence of oxygen, in both sunlight and darkness, to give benzophenone and a trisulfide. The other thiones were stable in the dark in benzene solution, but were readily converted to the corresponding ketone, sulfur and sulfur dioxide in the presence of sunlight. For nineteen years thereafter, interest in this area of photochemistry lay dormant, while interest in the photochemistry of ketones flourished.

Since 1962, an increasing enthusiasm to study the photochemistry of aromatic thioketones has been noticeable and many interesting reactions have been reported namely: photooxidation (13), photoreduction (13,14), photocycloaddition (15-22) and photocycliza-

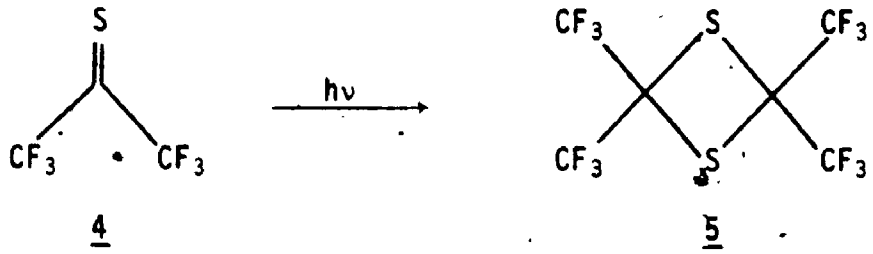
tion (23).

De Mayo and Schizuka were the first to report a detailed kinetic study of an aromatic thioketone (24). They investigated the photocycloaddition of thiobenzophenone to acrylonitrile at 366 and 550 nm and provided evidence that the reactive state at 366 nm is the second excited (π,π^*) singlet (24), while that at 550 nm is the lowest triplet (n,π^*) (25).



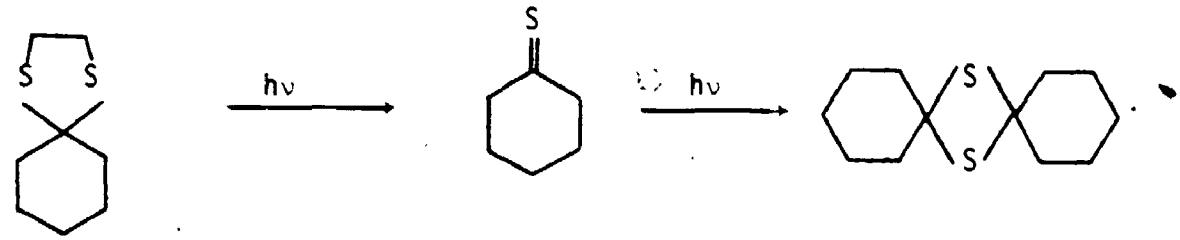
In contrast, aliphatic and alicyclic thioketones have been little investigated. This is probably due to the fact that thiocarbonyl compounds with an α-hydrogen atom undergo tautomerism to the more stable corresponding enethiol (26).

The published work to date deals with the photodimerization of perfluorothioketones (4 for instance) (27), the formation of

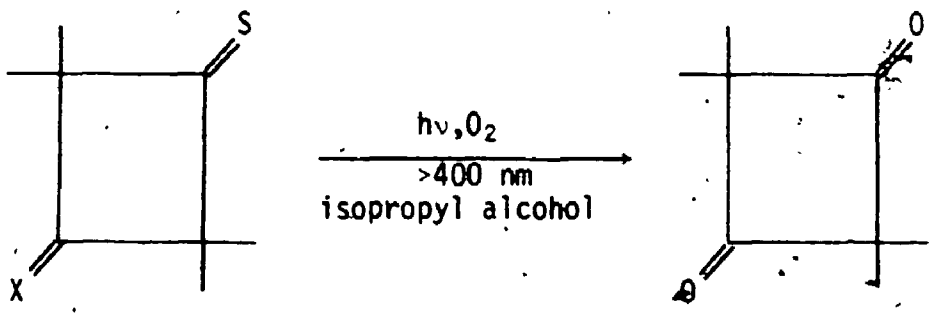


4 5

cyclohexanethione dimer 8 by photolysis of cyclohexanone dithioethyleneketal 6 (28), cyclohexanethione 7 being the presumed intermediate, and the photooxidation of tetramethyl-3-thio-1,3-cyclobutanedione 9a and tetramethyl-1,3-cyclobutanedithione 9b (29).



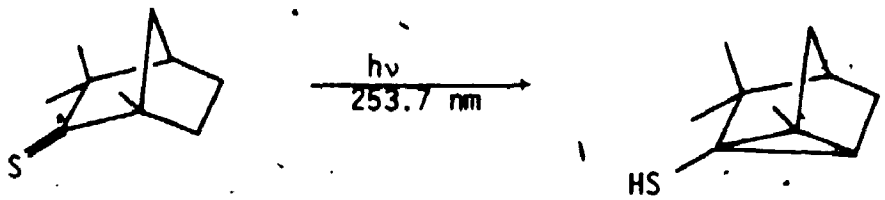
6 7 8



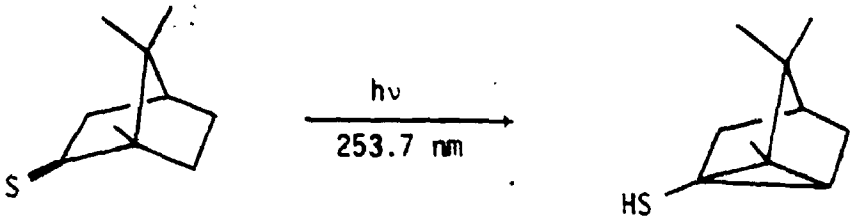
9a; X=O
b; X=S

10

Two independent studies on the photochemistry of non-aromatic thioketones have been initiated in our laboratory. Blackwell and de Mayo investigated the photochemistry of thiofenchone 11 and thiocamphor 13 and reported (30) a new class of reaction, cyclopropane formation which appears to be of very rare occurrence in carbonyl photochemistry.



11 12



13 14

Adamantanethione 15, was chosen (symmetrical molecule) to study the photocycloaddition and photoreduction reactions of alicyclic thiocarbonyl compounds.

(b) Photochemistry of Adamantanethione

Spectroscopic Properties

As a preliminary to the understanding of the reaction mechanisms involved, it was necessary to know something concerning the relevant, in this case the low-lying excited states.

The absorption spectrum of adamantanethione in cyclohexane is shown in Figure 1. Two main bands, one centered at 240 nm, with ϵ = 13,000, and another low intensity absorption centered at 500 nm, are observed. Liao (31) established that these absorption bands are the $S_o \rightarrow S_2$, (presumably π,π^*) and $S_o \rightarrow S_1$, (n,π^*) transition respectively. It has been found, too, by Liao and Paszyc (31) that the bright orange emission observed from adamantanethione (λexcitation 465 and 265 nm) in a glassy matrix at 77°K is phosphorescence, and this emission has a lifetime of 120 and 110 μsec in EPA and hydrocarbon matrices respectively (E_T = 52.6 and 52.0 kcal/mole in EPA and hydrocarbon matrices respectively) and is quenched by cyclooctatetraene. Based on the above observations, they described

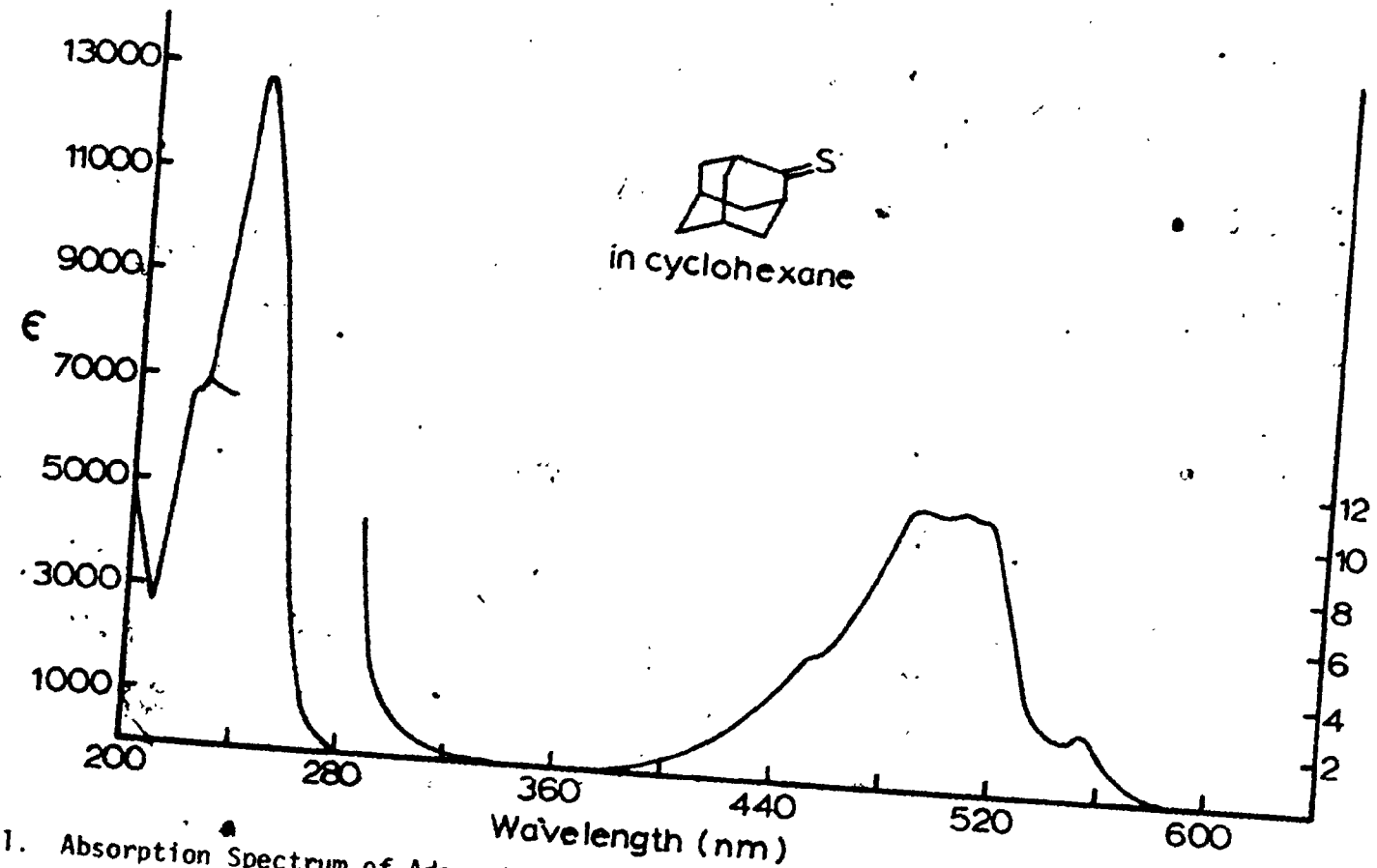
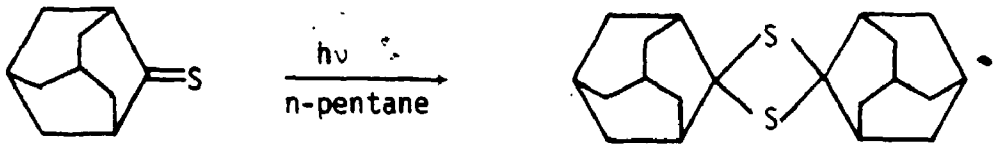


Figure 1. Absorption Spectrum of Adamantanethione in Cyclohexane.

the lowest triplet state of adamantanethione as n,π*. They also found what seems to be the n→π*, $S_0 \rightarrow T$ absorption at 545 nm with an extinction coefficient of ∿3.0.

Photochemical Reactions

Liao and de Mayo (32) found that irradiation of adamantanethione in n-pentane (253.7 nm) gives the dimer 16. The same product was obtained in benzene solution with light of longer wavelength (>420 nm), but the reaction was very much slower. Mechanistic studies were not carried out.

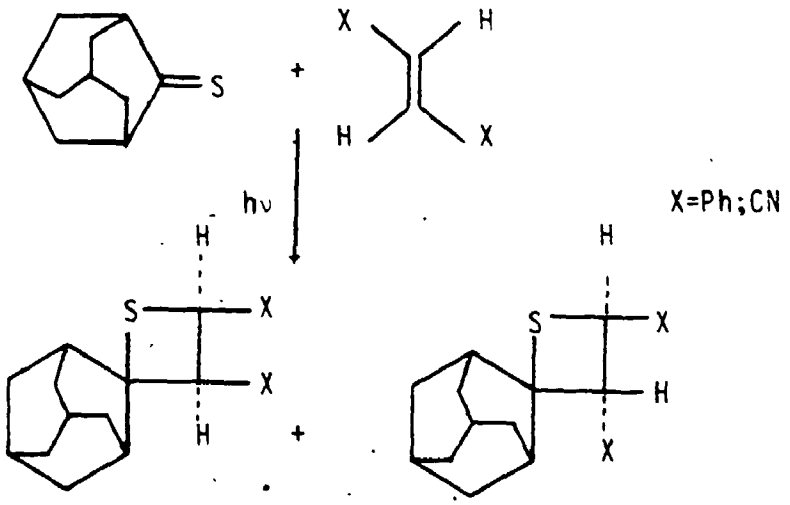


15 16

The photochemistry of adamantanethione in the presence of several olefins was also studied by Liao (31,32). In all cases excitation was of the n,π* transition. With ethyl vinyl ether adamantanethione yields the thietane 17. Similarly, thietane 18 was obtained when 1,1-diphenylethylene was used as substrate.

17 18

In the case of trans-stilbene and fumaronitrile, however, stereoisomeric thietanes were formed (19 and 20) and in both cases the starting olefins were found to be isomerized at the conclusion of the reaction.



19 20

Because of the general interest in thioketone photochemistry and the wavelength dependence reported (32) for dimer 16 formation, it was decided to study adamantanethione photochemistry in detail.

In the present work, the photocycloaddition reaction of adamantanethione to ethyl vinyl ether at 250 nm, the photoreduction with 2-adamantylthiol, the spectroscopic properties (flash photolysis) as well as a detailed kinetic study of photodimerization and photocycloaddition to ethyl vinyl ether at 250 and 500 nm were investigated. These findings are described in the following chapters.

CHAPTER 2

THE TRIPLET STATE OF ADAMANTANETHIONE STUDIED BY LASER FLASH PHOTOLYSIS

2.1 Introduction

Since the advent of photochemistry as a separate branch of chemistry, there has been a need for a method whereby chemists could study short-lived photochemically produced intermediates. In 1949, Norrish and Porter (33) described an apparatus that was partially able to fulfill this need. The general principle was to create the transient with a very intense light of brief duration (microsecond) and to study the return of the system to equilibrium by absorption spectroscopy. Since then, this so-called conventional flash photolysis technique has been applied to a variety of problems. For example, Bell and Linschitz (34) investigated the decay kinetics of 1-naphthaldehyde and benzophenone triplet states in benzene solution containing hydrogen donors, and they reported the absorption spectrum of the ketyl radical (Ph_2C-OH).

However, the lowest excited singlet (S_1) states of polyatomic molecules have lifetimes too short for detection by the conventional flash method and it became clear that extension of the method to shorter times would have very wide applications.

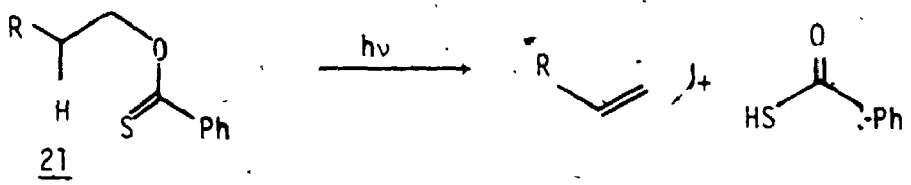
The discovery of the laser (35) provided scientists with a new source of light. The coherence, monochromaticity, power, collimation, polarization and temporal behavior of lasers opened new

ranges of time for the study of interaction of light with matter.

One of the sensational applications of lasers in chemistry has been the extension of Norrish and Porter's flash kinetic spectroscopy techniques from the microsecond timescale to the nanosecond and picosecond timescales. Many authors have already used the nanosecond timescale for flash kinetic studies (36-38).

Kemp and de Mayo (39) were the first to report the detection of transients in thiocarbonyl laser flash photolysis. Both thiobenzophenone and Michler's thione triplets were characterized.

Soon after, Barton and coworkers (40) reported the mechanism of thiobenzoic acid O-ester 21 photolysis and provided evidence from nanosecond flash photolysis studies that the reactive



21

species is the n,π* triplet state.

2.2 The Triplet State of Adamantanethione

The aim of our study was to detect and characterize the triplet state of adamantanethione whose photochemistry had been thoroughly investigated as a part of this project.

No transient absorptions were observed by conventional spectrographic flash photolysis of 10^{-4} - 10^{-3} M solutions of adamantanethione in n-hexane (41). We therefore pursued the study in detail using laser flash photolysis in the nanosecond range.

While aromatic thiones exhibit absorption in a region (42) which includes the emission from a ruby laser (347 nm) (39),

adamantanethione shows absorption at 265 and 530 nm, wavelengths at which the quadrupled and doubled neodymium laser emits. Using the nanosecond flash photolysis system already described (43), we have been able to detect a short-lived transient species from adamantanethione at room temperature (44). The evidence suggest that this short-lived absorption is attributable to the triplet state of adamantanethione.

Photolysis of degassed n-hexane solutions (0.19 - 5.05 x 10^{-3} M) of the thione gave rise to the same short-lived transient whether excitation was conducted at 265 or 530 nm. This species absorbed in the region 280-350 nm and presumably at shorter wavelengths, but here the ground state absorption of the thione interfered. The transient decayed with first order kinetics, and the rate of decay was dependent on the thione concentraction. From these results a self-quenching rate constant of 9.9 ± 0.5 x 10^9 M^{-1} sec^{-1} could be extracted. Thus in low-viscosity solvents, the self-quenching process becomes important at concentrations of starting material higher than 10^{-4} M. Furthermore, the observed self-quenching of this species rather excludes the possibility that it is due to an excimer. Extrapolation to infinite dilution gave a unimolecular rate constant for decay of 6.8 ± 0.3 x 10^5 sec^{-1}. This lifetime differs (shorter) by a factor of about two orders of magnitude from that measured from emission studies at 77°K (42). The decay rate of the absorption was constant, within experimental error, throughout the wavelength region investigated, indicating that only one short-lived species was being monitored.

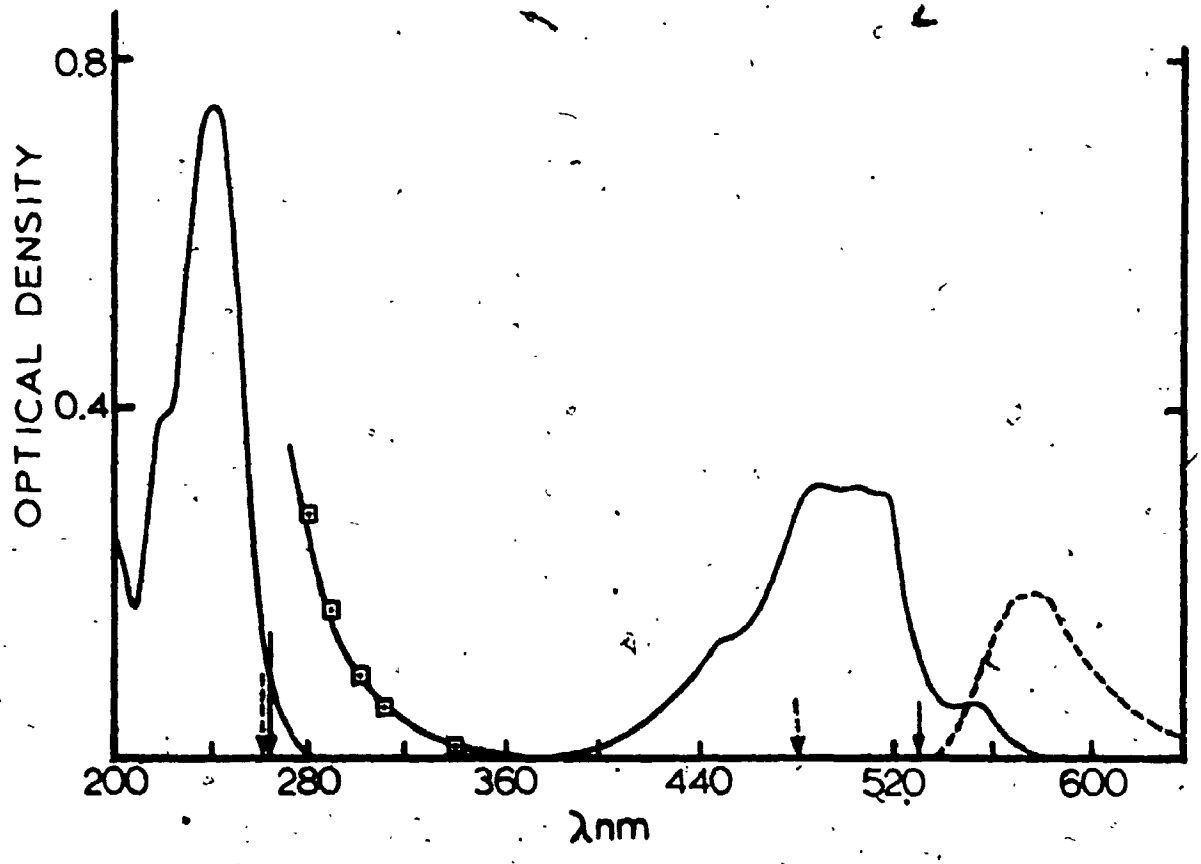


Figure 2. (-) Ground state absorption of adamantanethione; (⊡) triplet-triplet absorption; (---) phosphorescence of adamantanethione. Solid arrows: laser excitation; broken arrows: excitation for phosphorescence emission.

Table 1. The Concentration Effect of Adamantanethione on the Lifetime of the Triplet State

Concentration $X10^3(M)$	λexcitation (nm)	Optical Path (cm)	$1/\tau X10^{-7}(sec^{-1})$
0.190	265	5	0.23
0.315	265	5	0.43
0.500	265	5	0.71
0.950	265	1	1.13
1.26	530	5	1.35
1.30	265	1	1.23
1.57	265	1	1.60
1.97	530	5	2.08
2.60	265	1	2.77
5.05	530	5	4.55

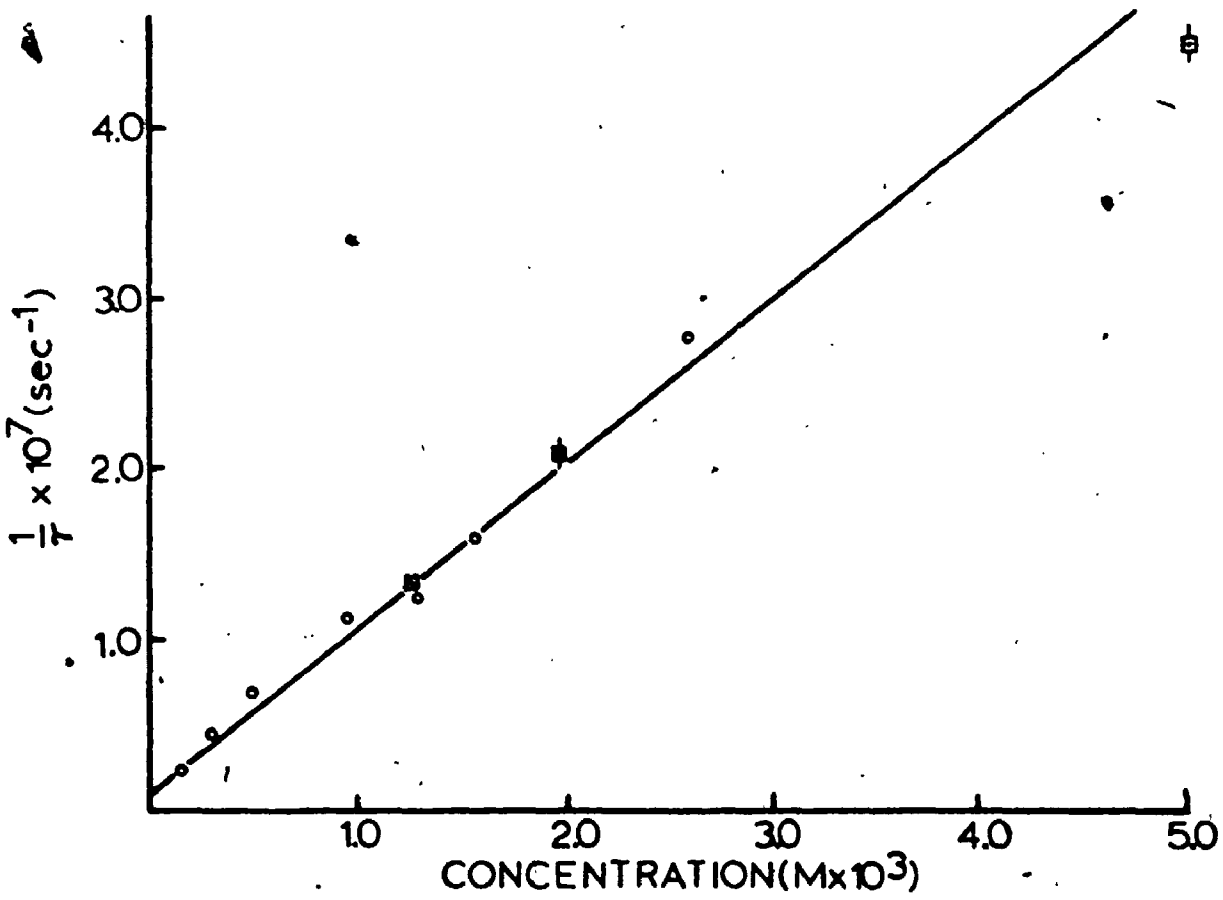


Figure 3. Triplet lifetime as a Function of Adamantanethione concentration. (o) Excitation at 265 nm; (⊡) Excitation at 530 nm.

The addition of increasing concentrations of 1,1'-azoisobutane [E_T = 53 ± 3 kcal/mole (45)] led to kinetic quenching of the species from adamantanethione. The choice of quencher was dictated by relative absorption problems, and by the difficulty in finding molecules having, particularly for steady state kinetics, low absorption in the 250-265 nm region. It was also necessary that they have triplet energies below and singlet energies above those of adamantanethione. From these studies, a quenching rate constant of $2.8 \pm 0.1 \times 10^8$ M^{-1} sec^{-1} was obtained (at 530 nm). The quenching rate which is significantly less than diffusion-controlled, suggests that the triplet energy of 1,1'-azoisobutane is indeed within the limits designated (45), i.e. triplet energy transfer to 1,1'-azoisobutane is slightly endothermic. Furthermore, it has been shown (46) that the triplet state of thiobenzophenone (E_T = 40.6 kcal/mole (42)) is not quenched by 1,1'-azoisobutane (E_T = 53 ± 3 kcal/mole (45)) indicating that the quenching observed in the present study is not chemical in nature thus clearly establishing energy transfer as the quenching mechanism.

The above observations, together with the fact that the upper limit for the lifetime of the first excited singlet state of adamantanethione is ∿12 nsec (see Chapter 3) leave no doubt that the transient observed is due to absorption by the lowest triplet state of adamantanethione.

The relative triplet yield was measured (see Experimental) by irradiating a solution of adamantanethione (1.43×10^{-3} M) in n-hexane both at 265 (S_2) and 530 nm (S_1) and was found to be 1 ± 0.1.

Table 2. Quenching of the Triplet Lifetime of Adamantanethione with 1,1'-Azoisobutane

Quencher (M)	τ (nsec)	$1/\tau \times 10^{-6}$ (sec^{-1})
0.000	166	6.2
0.013	99	10.1
0.020	83	12.0
0.028	71	14.0
0.040	55	18.1

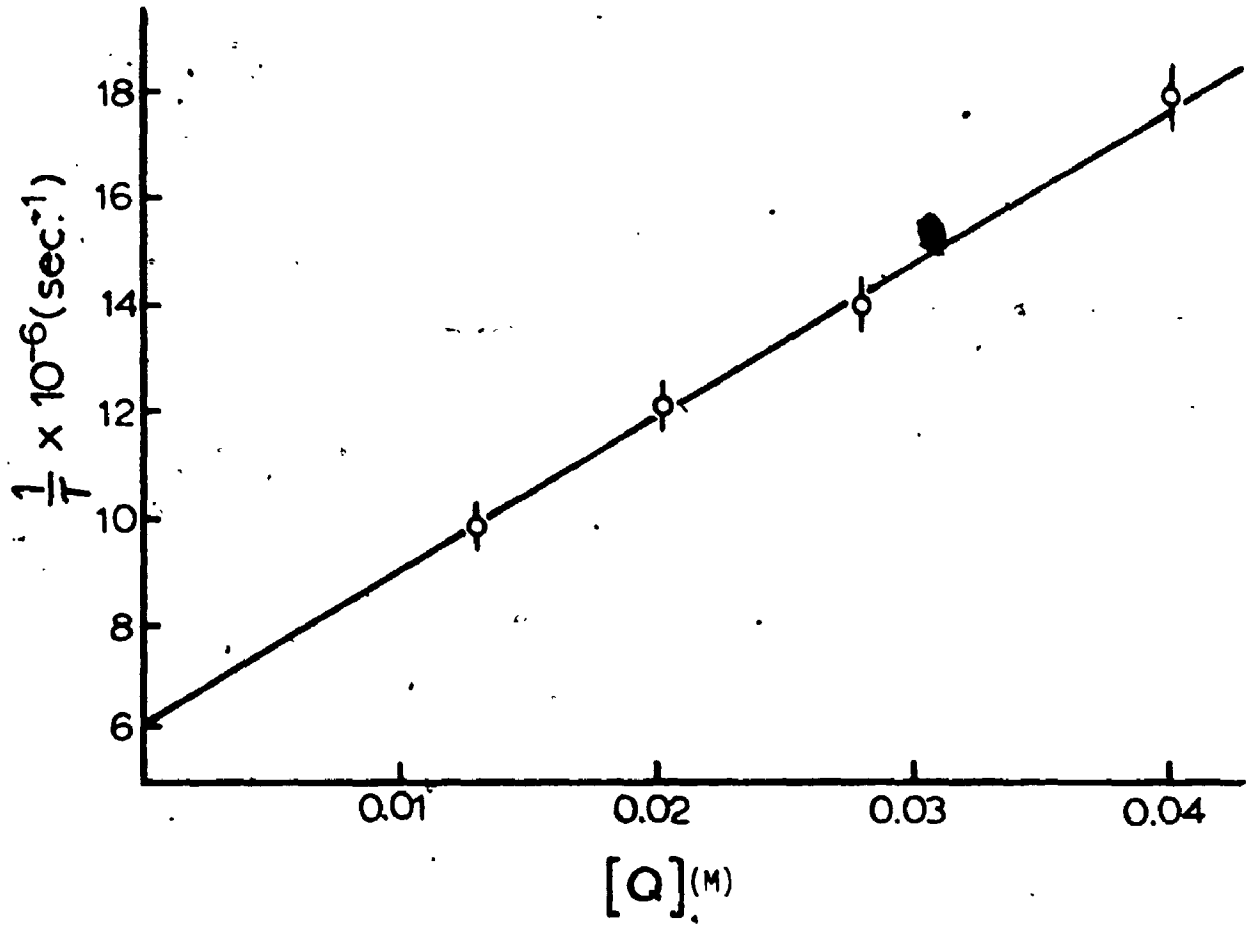


Figure 4. Quenching of the Triplet lifetime of Adamantanethione with 1,1'-Azoisobutane.

The dependence of the observed rate constant of decay on the initial concentration provides unequivocal evidence for direct interaction of adamantanethione triplets and ground state molecules presumably to give a triplet excimer or 1,4-diradical (see Chapter 3). The formation of the dimer 16 as the major product of irradiation of adamantanethione (31,32), is consistent with this suggestion.

It is clear from this study and from earlier studies (39,40), that self-quenching, a process already proposed in ketone photochemistry (47, 48 and 49) is also general for thioketone triplets.

CHAPTER 3

THE MECHANISM OF PHOTODIMERIZATION AND PHOTOCYLCOADDITION OF ADAMANTANETHIONE TO ETHYL VINYL ETHER AT 500 nm

3.1 The Multiplicity of the Reactive Species

The photocylcoaddition of adamantanethione to ethyl vinyl ether was chosen for kinetic studies because the latter compound has high solubility in benzene and the reaction at 500 nm was clean giving essentially one photoadduct 17 in good yield (72%) (31).

When a benzene solution of adamantanethione (0.2 M) and ethyl vinyl ether (2.0 M) was used, the quantum yield for thietane 17 formation was found to be 4.6×10^{-4} (3.7×10^{-4} in acetonitrile). The reaction could be sensitized by triplet sensitizers such as benzophenone, Michler's ketone and triphenylene and also quenched to an extent of 50% by triplet quenchers, 9-methylanthracene and cyclooctatetraene at concentrations of 0.1 M and 0.4 M respectively (31) (see Figure 5).

Similarly when a benzene solution of adamantanethione (0.2 M) was irradiated at 500 nm, the quantum yield for dimer 16 formation was found to be 1.4×10^{-4} (1.0×10^{-4} in acetonitrile). The photodimerization could also be sensitized by triplet sensitizers such as benzophenone and Michler's ketone.

The above results of sensitization and quenching experiments clearly indicate that the lowest triplet state of adamantanethione is responsible for both the photodimerization and the photocylcoaddition to ethyl vinyl ether.

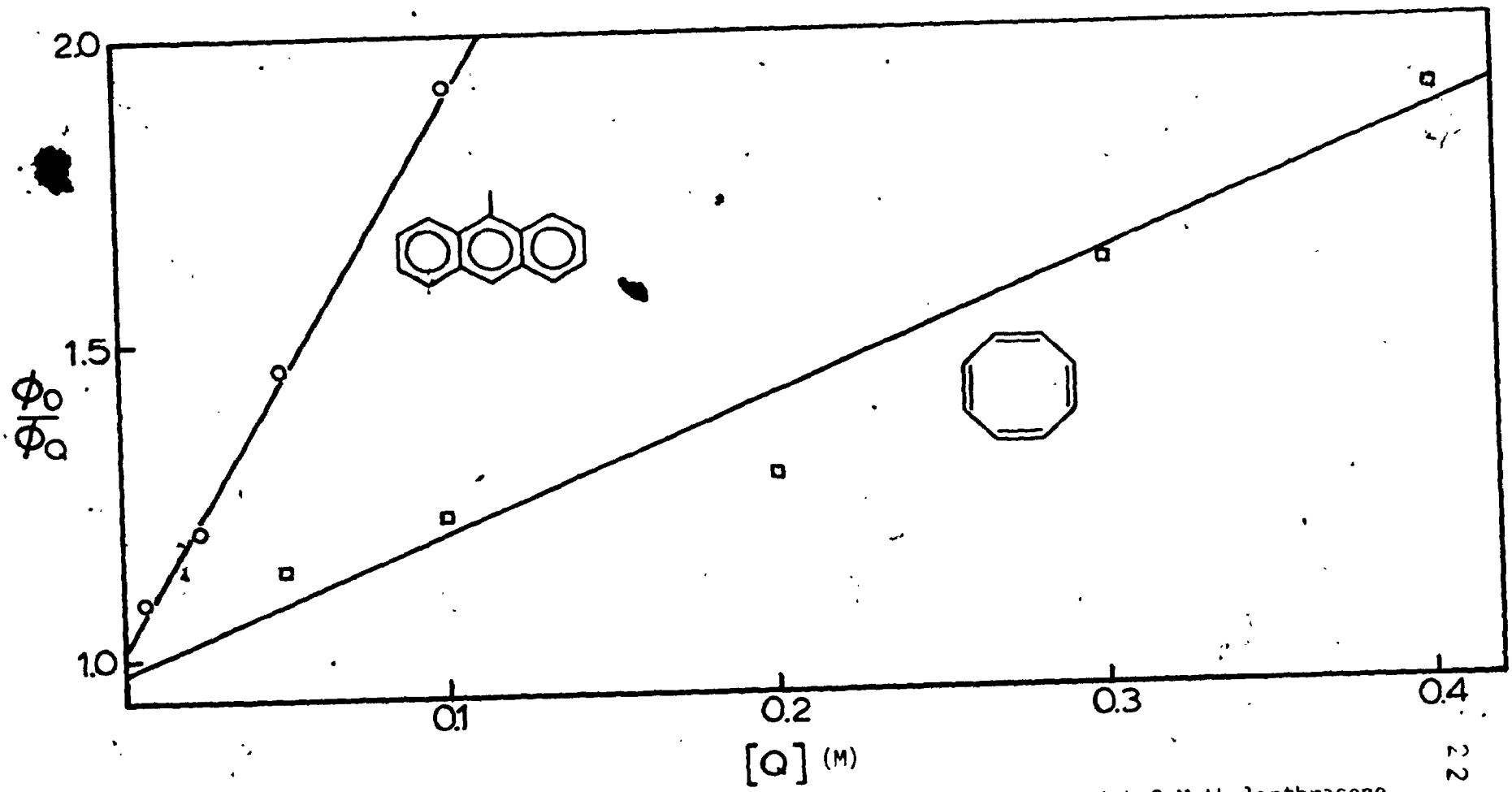


Figure 5. Stern-Volmer Plots of the Quenching of Thietane 17 Formation with 9-Methylanthracene and Cyclooctatetraene.

3.2 Reaction and Decay Rate Constants

We have reported in Chapter 2 (a conclusion based on flash photolysis experiments) that the triplet thione molecules undergo quenching by ground state molecules at a near diffusion-controlled rate. If the quenching of the triplet and dimerization of adamantanethione have a common intermediate, then the partition between the intermediate(s) on going to the dimer and those regenerating ground state adamantanethione must be in favor of the latter process by several orders of magnitude since the dimerization is a very inefficient process.

$$T_1 + S_o \xrightarrow{k_1} M_1$$

$$M_1 \xrightarrow{k_2} S_o + S_o$$

$$M_1 \xrightarrow{k_3} \text{dimer}$$

In the above equations, S_o and T_1 stand respectively for the ground state and the lowest triplet state of adamantanethione. M_1 may be a triplet excimer or a 1,4-biradical. The rate k_1 is that for the trapping of the triplet by ground-state thione molecules (diffusion-controlled), and k_2 and k_3 are the rate constants for the fragmentation to the ground state thione molecules and the formation of dimer from M_1 respectively. Therefore, from the lowness of the quantum yield of dimer formation and the efficient intersystem-crossing of the thione (see later), an interpretation of the energy wasting process is that $k_2 >> k_3$, i.e. the intermediate M_1 has a low energy of activation for dissociation to ground state thione

molecules than for formation of dimer. It has been reported in many cases (50, 51 and 52) that 1,4-biradicals have greater tendency to undergo cleavage than a coupling reaction.

Further evidence for the quenching process of the triplet is provided by the study of the effect of concentration of adamantanethione on the quantum yield of thietane 17 formation (32). The results shown in Figure 6 confirm the quenching of adamantanethione triplet by ground state molecules. It follows that when adamantanethione is irradiated at 500 nm in the presence of ethyl vinyl ether, both the olefin and ground state thione compete for the reactive triplet. As will be shown later, the photocycloaddition to olefins is a stepwise process; hence our observations at 500 nm appear to require the following extensive, but minimum set of equations

$$T_1 + S_o \xrightarrow{k_1} M_1$$

$$M_1 \xrightarrow{k_2} S_o + S_o$$

$$M_1 \xrightarrow{k_3} \text{dimer}$$

$$T_1 \xrightarrow{k_4} S_o$$

$$T_1 + O \xrightarrow{k_5} M_2$$

$$M_2 \xrightarrow{k_6} S_o + O$$

$$M_2 \xrightarrow{k_7} \text{thietane } 17$$

$$T_1 + Q \xrightarrow{k_8} S_o + Q^3$$

where Q, Q^3 and O represent the ground and the triplet states of

molecules than for formation of dimer. It has been reported in many cases (50, 51 and 52) that 1,4-biradicals have greater tendency to undergo cleavage than a coupling reaction.

Further evidence for the quenching process of the triplet is provided by the study of the effect of concentration of adamantanethione on the quantum yield of thietane 17 formation (32). The results shown in Figure 6 confirm the quenching of adamantanethione triplet by ground state molecules. It follows that when adamantanethione is irradiated at 500 nm in the presence of ethyl vinyl ether, both the olefin and ground state thione compete for the reactive triplet. As will be shown later, the photocycloaddition to olefins is a stepwise process; hence our observations at 500 nm appear to require the following extensive, but minimum set of equations

$$T_1 + S_o \xrightarrow{k_1} M_1$$

$$M_1 \xrightarrow{k_2} S_o + S_o$$

$$M_1 \xrightarrow{k_3} \text{dimer}$$

$$T_1 \xrightarrow{k_4} S_o$$

$$T_1 + O \xrightarrow{k_5} M_2$$

$$M_2 \xrightarrow{k_6} S_o + O$$

$$M_2 \xrightarrow{k_7} \text{thietane } \underline{17}$$

$$T_1 + Q \xrightarrow{k_8} S_o + Q^3$$

where Q, Q^3 and O represent the ground and the triplet states of

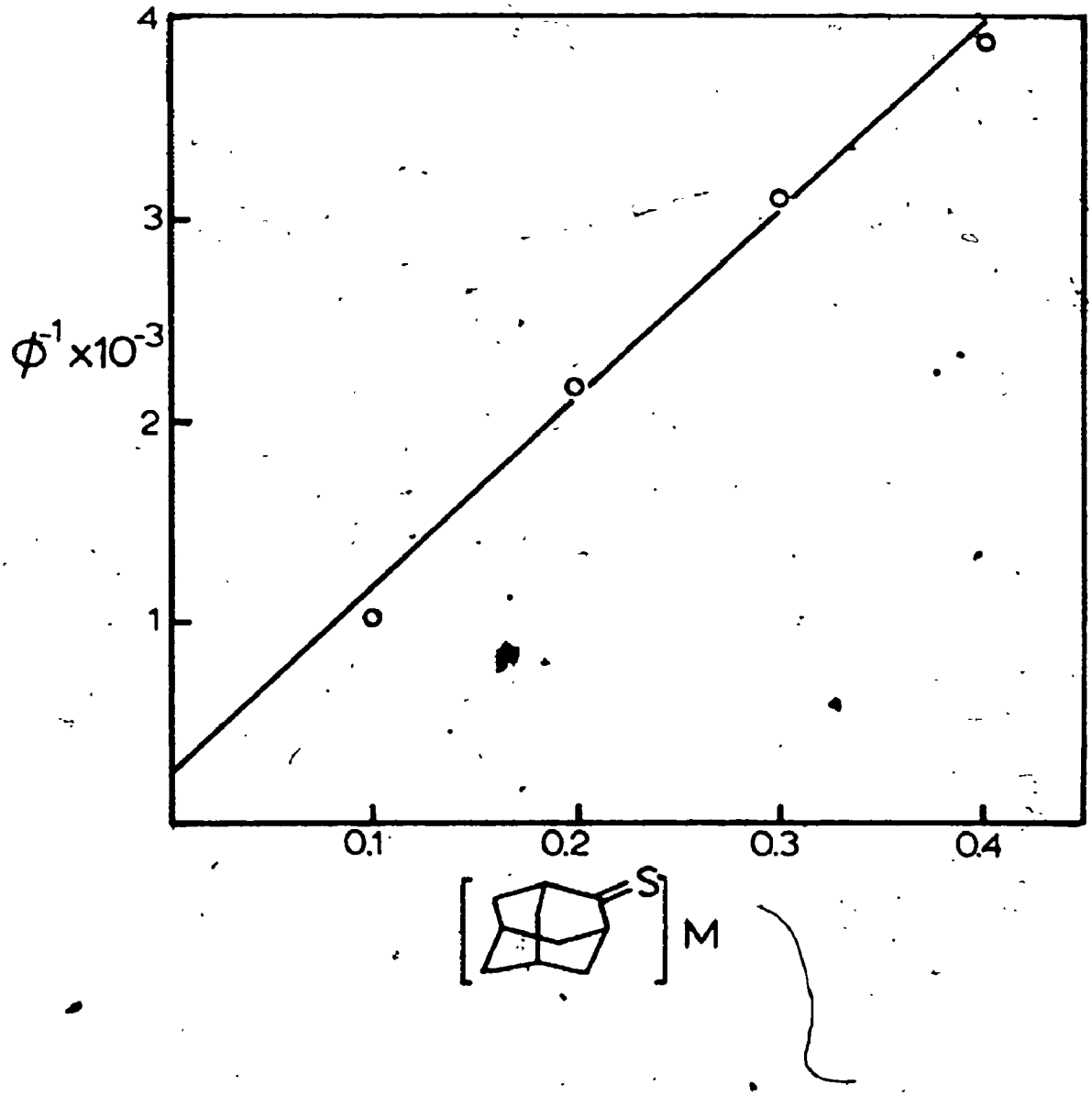


Figure 6. The effect of concentration of adamantanethione on the quantum yield of thietane 17 formation.

quencher and the ground state of olefin (ethyl vinyl ether in the present case) respectively, k_4 is the rate constant for the unimolecular decay of the lowest triplet state of adamantanethione, k_5 is the rate constant for trapping of the triplet by olefin, k_6 and k_7 are the rate constants for the fragmentation to the ground state thione and olefin and the formation of thietane 17 from the metastable intermediate M_2 (see later) respectively and k_8 is the rate constant for bimolecular quenching.

From the above equations, the usual steady state treatment for the addition of adamantanethione triplet to the olefin gives the expression

$$\Phi^{-1} = \text{constant} \times \left[1 + \left(\frac{k_4 + k_1[S_o]}{k_5[O]}\right)\right] \quad (1)$$

where $[S_o]$ as well as $[O]$ are, respectively, the concentration of thioketone and olefin. Dilution experiments using different concentrations of ethyl vinyl ether and keeping the concentration of adamantanethione constant (0.2 M) were carried out (31). A linear plot of Φ^{-1} against $[O]^{-1}$ was obtained (see Figure 7) which has an intercept of 580 ± 80 and a slope of 3423 ± 140 M. From these values the parenthetical term in equation (1) can be extracted. Since k_1 and k_4 have been measured directly from flash experiments (see Chapter 2), k_5 can be calculated and has a value of $1.71 \pm 0.3 \times 10^8$ M^{-1} sec^{-1} (we make here the explicit assumption that k_1 equals to 5×10^9 M^{-1} sec^{-1}, the diffusion-controlled rate value in benzene (53,54). The value of k_5 may be reached by another route. From the intercept and the slope

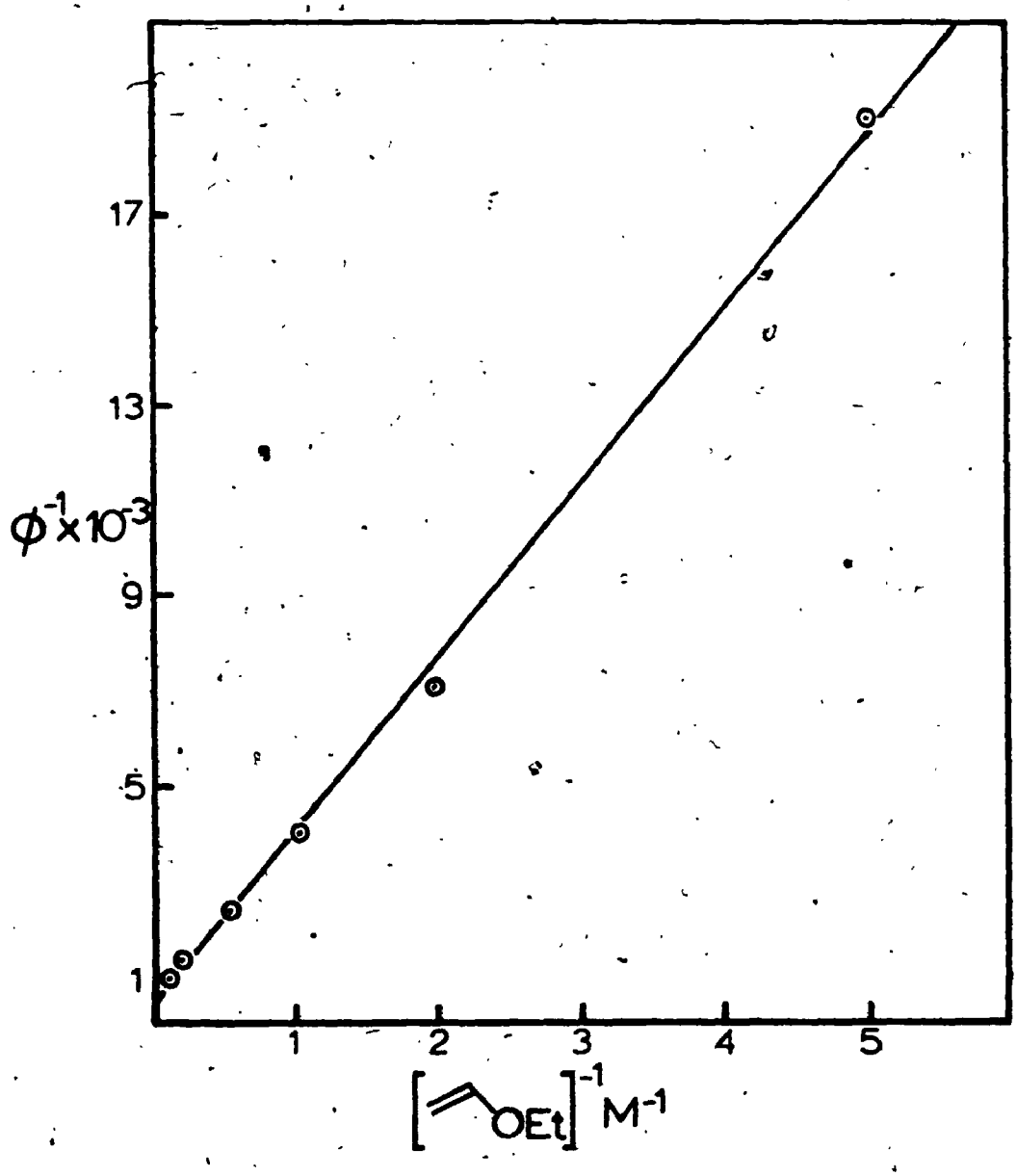


Figure 7. The Effect of Concentration of Ethyl Vinyl Ether on the Quantum Yield of Thietane 17 Formation.

(32) of the plot shown in Figure 6, and inserting the values of k_1, k_4 and $[O]$ = 2.0 M into equation (1), k_5 can be calculated and has a value of 8.0 ± 0.4 x 10^7 M^{-1} sec^{-1}.

The normal Stern-Volmer expression for the quenching of thietane 17 formation is given by

$$\Phi_o/\Phi_Q = 1 + \frac{k_8[Q]}{k_4 + k_1[S_o] + k_5[O]} \quad (2)$$

where Φ_Q and Φ_o are the quantum yields of thietane formation with and without quencher respectively, and $[Q]$ is the concentration of the quencher. The slope of the Stern-Volmer plot is equal to $k_8/(k_4 + k_1[S_o] + k_5[O])$. From the quenching experiments varying the concentration of the quencher and keeping the concentration of adamantanethione and olefin constant (0.2 M) and (2.0 M) respectively, the Stern-Volmer slopes (see Figure 5) were found by using the least squares method to be 9.14 M^{-1} and 2.17 M^{-1} for 9-methylanthracene and cyclooctatetraene, respectively. The plots were linear up to a value of about 2 implying a triplet reaction up to at least 50% quenching.

Using the values of the Stern-Volmer slopes and the previously measured values of k_1 and k_4, as well as the calculated value of k_5 (1.7 x 10^8 M^{-1} sec^{-1} for instance), the bimolecular quenching rate constant k_8 may be determined and has a value of 1.2 ± 0.6 x 10^{10} M^{-1} sec^{-1} and 2.9 ± 0.1 x 10^9 M^{-1} sec^{-1} for quenching by 9-methylanthracene and cyclooctatetraene respectively. These values are in agreement with an exothermic triplet energy transfer from adamantanethione (E_T = 52 kcal/mole) to 9-methylanthracene

(E_T = 41.9 kcal/mole (55); 40.6 kcal/mole (56)) and cyclooctatetraene (E_T < 40 kcal/mole (57)).

3.3 The Lifetime of the S_1 State of Adamantanethione

The lifetime measurements for the excited singlet states of organic compounds have been reported in many instances. For compounds exhibiting fluorescence emission at room temperature (58), singlet lifetimes (τ_s) have been measured by monitoring the fluorescence decay via the single photon counting technique (59). Dubois et al. (60, 61 and 62) have shown that electronic energy transfer from the excited singlet state of a donor molecule, to that of an acceptor molecule, is diffusion-controlled, when an acceptor having a low extinction coefficient, such as biacetyl is used. Under these conditions, the long-range singlet-singlet energy transfer due to dipole-dipole interaction of the transferring species may be avoided. The lifetime of the second excited singlet state of thiobenzophenone, for instance, has been estimated by this method and was reported to be in the order of 10^{-11} sec (24).

In the case of adamantanethione neither fluorescence (63) nor reactions originating from the lowest excited singlet state could be detected. This precluded the use of the above mentioned methods for the lifetime estimation of the S_1 state and an indirect method was therefore attempted.

The upper limit for the quantum yield of fluorescence from a 5×10^{-3} M n-hexane solution of adamantanethione (λ= 531 nm) was found to be 3.6×10^{-4} (see Experimental) (the lowest detectable level by comparison with rhodamine B used as a standard (64)).

The radiative lifetime (τ^o) of the S_1 state of adamantanethione was calculated from the oscillator strength of the absorption band using equation (3) (65).

$$\tau_o = \frac{3.5 \times 10^8}{\bar{\nu}_m^2 \, \varepsilon_m \, \Delta\bar{\nu}_{\frac{1}{2}}} \qquad (3)$$

where $\bar{\nu}_m$ the mean frequency of the absorption band (in reciprocal centimeters), ε_m is the maximum extinction coefficient of the band and $\Delta\bar{\nu}_{\frac{1}{2}}$ is the half-width of the band in reciprocal centimeters. τ_o was found to be 3.3×10^{-5} sec.

The upper limit for the lifetime of the S_1 state of adamantanethione at a concentration of 5×10^{-3} M can therefore be calculated from equation (4) and has a value of approximately 12 nsec.

$$\Phi_{fl} = \frac{1}{\tau^o} \times \tau \qquad (4)$$

3.4 The Efficiency of Triplet Formation

In 1965 Lamola and Hammond (66) developed an elegant chemical method for determining the intersystem crossing efficiencies of triplet sensitizers. The method involves determination of the quantum yield of cis to trans isomerization of dienes. However, the above mentioned method cannot be applied to adamantanethione for the following reasons: firstly, thioketones were found to undergo both 1,2 and 1,4 photochemical addition to dienes (16), as well as thermal (67) 1,4 addition to dienes, secondly, the triplet energy of dienes is slightly above that of adamantanethione (cis-piperylene E_T =

56.9 kcal/mole).. Another approach was then attempted; this involved the comparison of the efficiencies of thietane 17 formation for the sensitized and non-sensitized reactions.

It was found by Liao (31) that the quantum yield of thietane formation sensitized by Michler's ketone [$\phi = 4.7 \times 10^{-4}$ when a benzene solution of adamantanethione (0.2 M), Michler's ketone (0.01 M) and ethyl vinyl ether (2 M) was used; λexcitation 366 nm] was identical with that of the reaction directly induced by light [$\phi = 4.6 \times 10^{-4}$ when a benzene solution of adamantanethione (0.2 M) and ethyl vinyl ether (2.0 M) was used; λexcitation 500 nm]. Since it is known that Michler's ketone has a triplet yield of unity (66), and that the concentration of adamantanethione is twenty times as great as that of Michler's ketone in the sensitized experiment, the energy transfer from the triplet Michler's ketone to the ground state thione would be expected to dominate the self-quenching process reported for Michler's ketone triplet (47, 48 and 68). The above results (equal efficiencies of thietane formation for the direct irradiation and sensitized reaction) seem to indicate that the triplet yield of adamantanethione is near unity. This was further supported by the use of triphenylene as sensitizer ($\Phi_{isc} = 0.95$) (69).

When a benzene solution of adamantanethione (0.2 M), triphenylene (0.01 M) and ethyl vinyl ether (2 M), was used (λ excitation 313 nm) the quantum yield of thietane 17, formation was found to be 4.7×10^{-4}. Once again the efficiency of the reaction was identical (within experimental error) whether the energy was

introduced into the molecule directly or via a sensitizer. However, adamantanethione was shown to quench triphenylene fluorescence at a rate close to diffusion-controlled (see Experimental). The results are shown in Table 3 and plotted in Figure 8. Since the intensity of the fluorescence is directly related to the quantum yield of fluorescence, one can obtain equation (5) after applying the usual Stern-Volmer expressions and steady state assumptions.

$$F_o/F = 1 + k_Q\tau[Q] \qquad (5)$$

where F_o and F represent the intensity of fluorescence in absence and presence of quencher respectively, k_Q is the bimolecular quenching rate constant, τ is the lifetime of the S_1 state of triphenylene (12.9 nsec; in benzene at 0.01 M concentration) and $[Q]$ is the concentration of the quencher (adamantanethione in the present case). From the slope of the Stern-Volmer plot, k_Q was found to be $2.44 \pm 0.1 \times 10^9\ M^{-1}\ sec^{-1}$, and at 0.2 M thione, 87% of triphenylene singlets are quenched by adamantanethione. It follows that the quantum yield (4.7×10^{-4}) obtained on sensitization of the photocycloaddition reaction with triphenylene can be rationalized in terms of Diagram 1. Adamantanethione triplet is being generated by two pathways (a) and (b). The contribution of path (a) to the measured quantum yield can be calculated as follows

$$\Phi(a) = \frac{4.6 \times 10^{-4} \times 87}{100} = 4.0 \times 10^{-4}$$

where 4.6×10^{-4} is the quantum yield of thietane formation upon

Table 3. Quenching of Triphenylene[+] Fluorescence by Adamantanethione

Thione conc. (M)	F	$(F_o/F - 1)^*$
0.05	437	1.478
0.10	273	2.967
0.15	194	4.582
0.20	144	6.521

+ Triphenylene concentration = 0.01 M (solvent : benzene)

* F_o = 1083

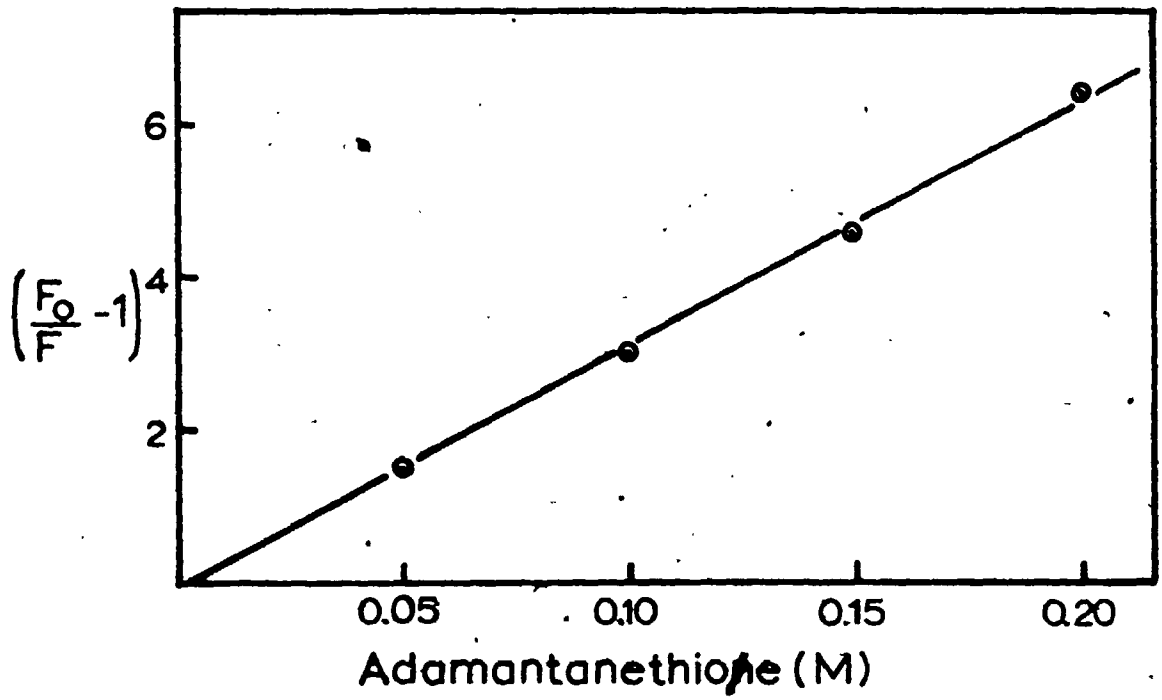


Figure 8. Stern-Volmer Plot of the Quenching of Triphenylene Fluorescence with Adamantanethione.

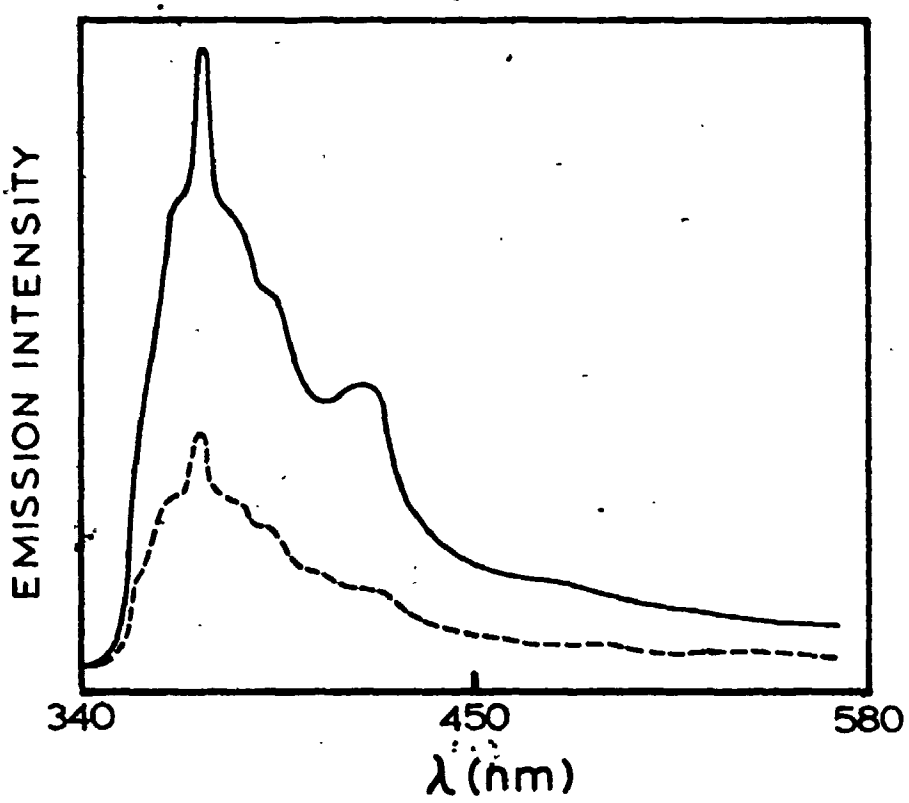


Figure 9. Quenching of Triphenylene Fluorescence by adamantanethione. (-) Triphenylene fluorescence in absence of thione; (---) in the presence of 0.05 M thione.

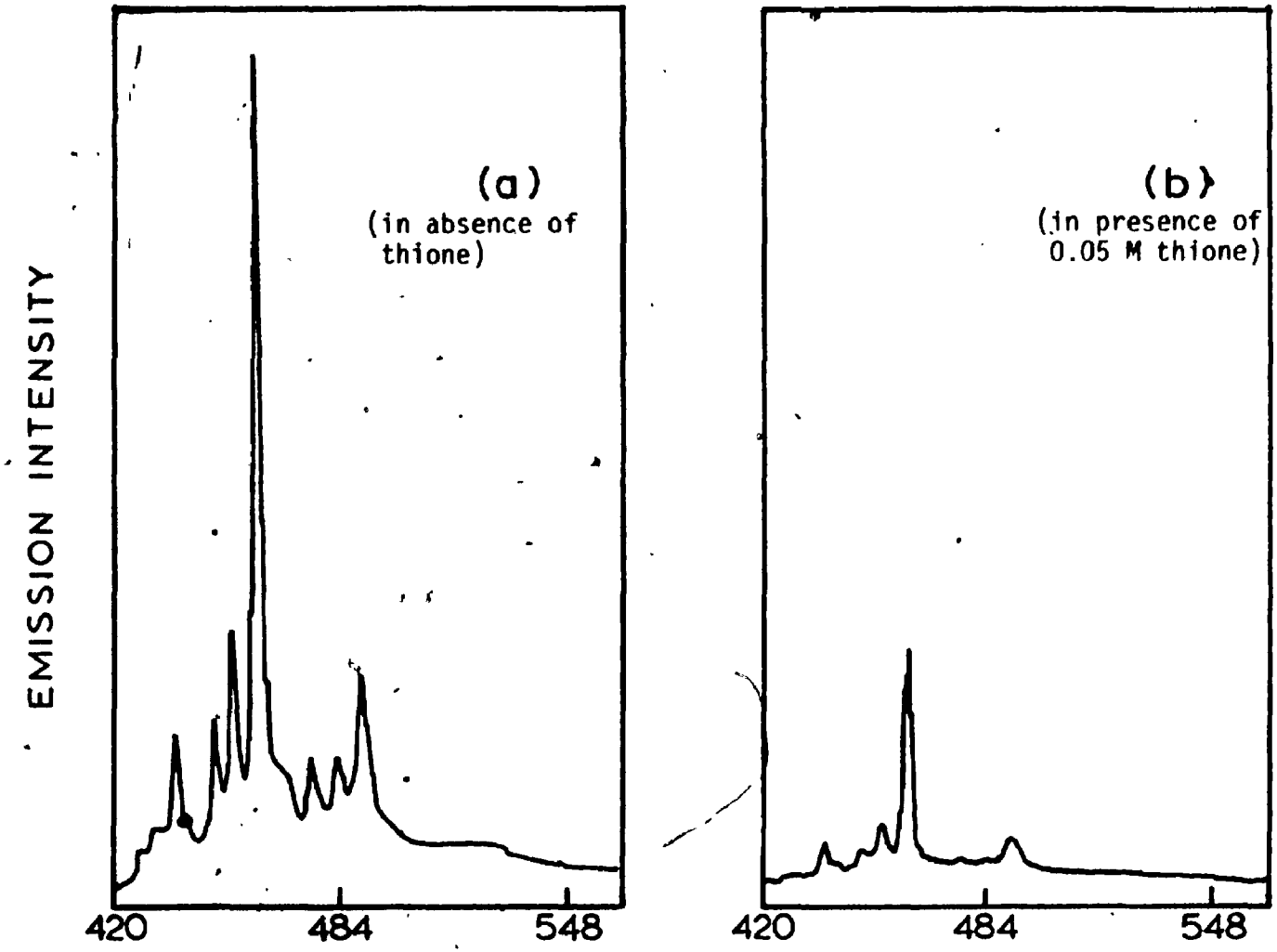


Figure 10. Quenching of triphenylene phosphorescence by Adamantanethione.

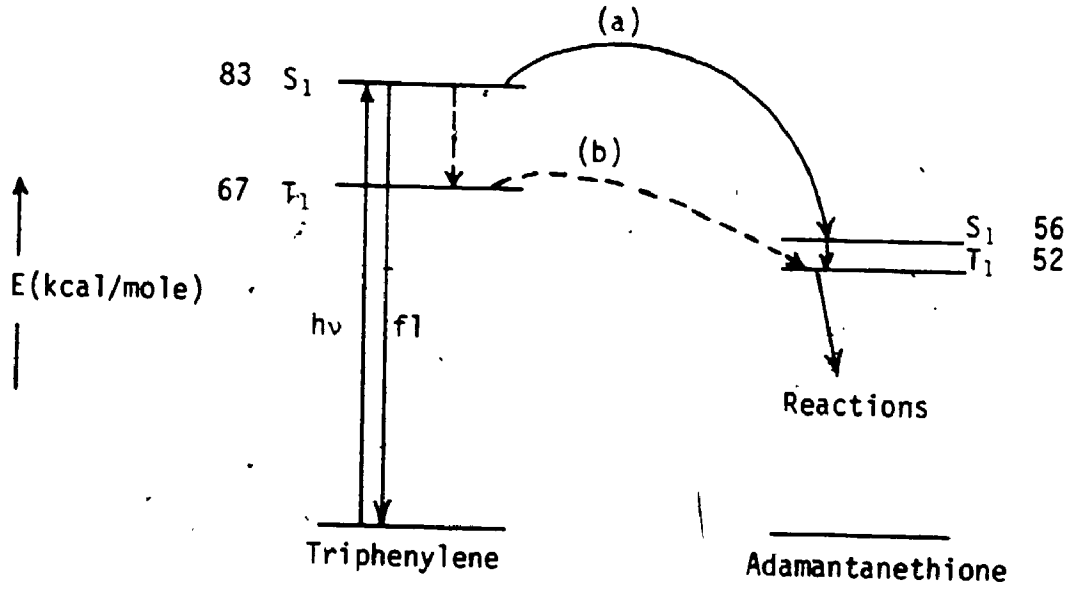

(a)
83 S_1
(b)
67 T_1
S_1 56
T_1 52
E(kcal/mole)
hν
fl
Reactions
Triphenylene
Adamantanethione

Diagram 1.

direct irradiation of a benzene solution of adamantanethione (0.2 M) and ethyl vinyl ether (2 M), and the contribution of path (b) is therefore given by

$$\Phi_{(b)} = 4.7 \times 10^{-4} - 4.0 \times 10^{-4} = 0.7 \times 10^{-4}$$

We make here the explicit assumption that no energy wasting processes take place between triphenylene and adamantanethione. Furthermore, it was found that the quantum yield of dimerization sensitized by Michler's ketone [4.0×10^{-4}, when a benzene solution of adamantanethione (0.2 M) and Michler's ketone (0.01 M) was used; λexcitation 366 nm] was close to that of the reaction directly induced by light [$\Phi = 1.4 \times 10^{-4}$, when a benzene solution of adamantanethione (0.2 M) was used; λexcitation 500 nm]. The rather large error could be due to thermal formation of the dimer (see Experimental).

The above results appear to require the following processes for the generation and fate of the S_1 state of adamantanethione.

$$S_o \xrightarrow{h\nu} S_1$$

$$S_1 \xrightarrow{k_9} S_0$$

$$S_1 \xrightarrow{k_{10}} S_o + h\nu'$$

$$S_1 \xrightarrow{k_{11}} T_1$$

where S_1 represents the first excited singlet state of adamantanethione, k_9 is the rate constant for the unimolecular decay of the S_1 state, k_{10} is the rate constant for fluorescence and k_{11}

is the rate constant for intersystem crossing.

We have ignored the possibility of quenching of the lowest singlet state of adamantanethione by ground state molecules. Whilst we have no direct method for excluding this possibility, it appears (from sensitization experiments) that the efficiency of this process is small with respect to intersystem crossing. The small energy difference between singlet and triplet of n,π* excited adamantanethione ($\Delta E_{ST} \sim 4$ kcal/mole) as well as the heavy atom effect of sulfur suggest a fast intersystem crossing process (70 and 71) supporting the above mechanism.

The lower limit to the value of k_{11} (intersystem crossing) can be estimated as follows: the upper limit to the lifetime of the S_1 state of adamantanethione was calculated to be 12 nsec and is given by the following expression

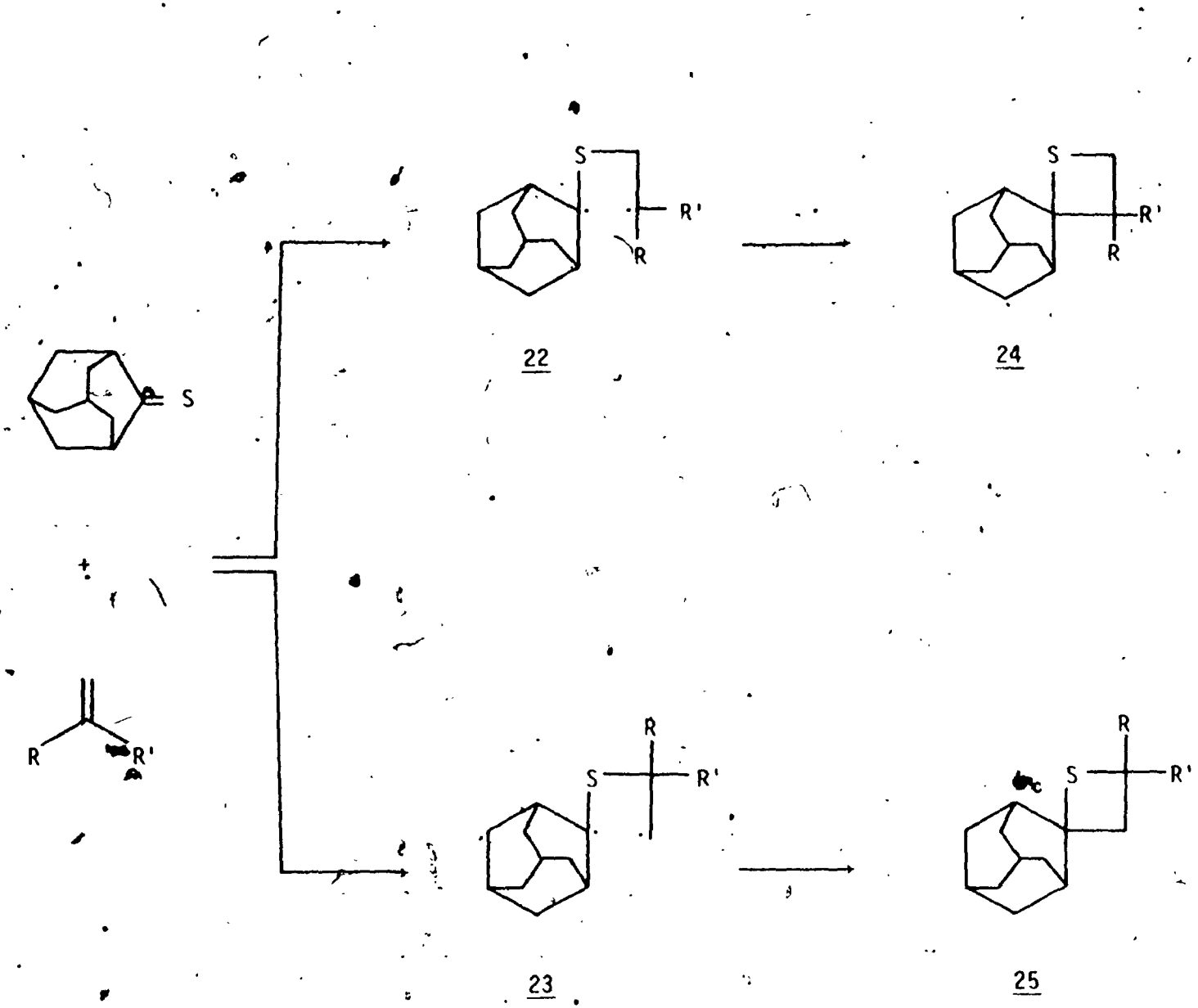
$$\tau_{\text{upper limit}} = \frac{1}{k_9 + k_{10} + k_{11}} \qquad (6)$$

if we make the assumption that k_9 is small relative to k_{11} (large energy gap between the S_1 and the ground state ($\sim$ 56 kcal/mole)), and insert the value of k_{10} previously calculated into equation (6) the lower limit to k_{11} can be determined and has a value of $\sim 10^8$ sec^{-1}.

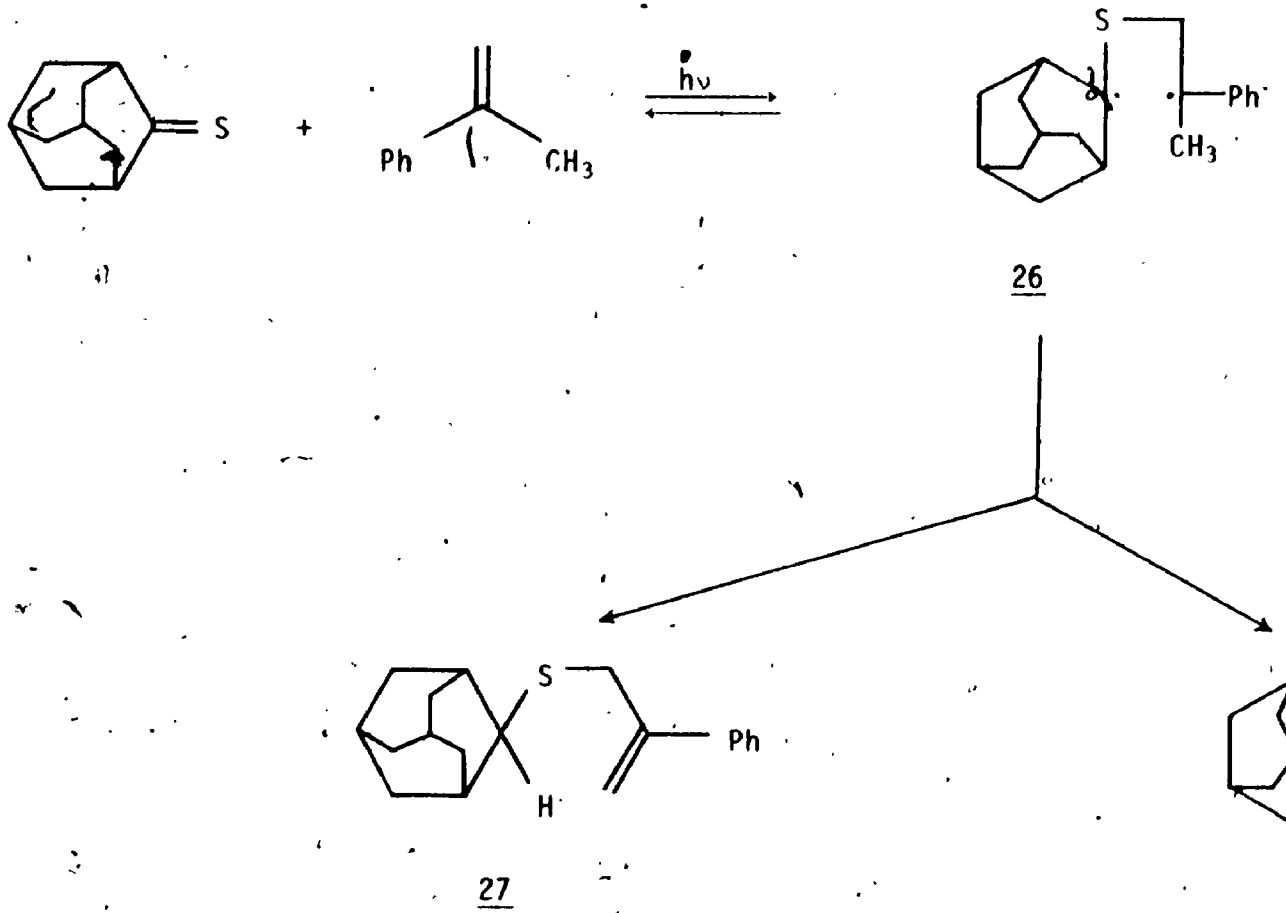
3.5 The Stepwise Nature of the Thietane Formation Process

Evidence for the involvement of 1,4-diradicals in the photoaddition of adamantanethione to olefins at 500 nm has been provided chemically (31). The photocycloaddition at long wavelength of adamantanethione to unsymmetrical olefins such as ethyl vinyl

ether, α-methylstyrene and 1,1-diphenylethylene may give two possible thietanes differing only in the disposition of the substituents on the thietane ring (24 and 25 see Scheme 1). However, essentially one isomer was produced in these cases. These results can be rationalized by the well-established mechanism for oxetane formation from a ketone and an olefin via a triplet state of the carbonyl compound (3). The attack by the electrophilic half vacant n orbital of the sulfur atom of the n,π* triplet state of adamantanethione on the double bond of the olefinic compound leads to the formation of a more stable 1,4-diradical which then dictates the disposition of the substituents on the thietane ring. The diradical 22 is more stable than the diradical 23 (see Scheme 1) since a tertiary radical (a secondary radical in the case of ethyl vinyl ether) is more stable than a primary one. However, formation of 23 in a slower process (relative to 22) followed by reversibility cannot be excluded. Thus the product 24 (not 25) having the substituents at the 3-position of the thietane ring is formed. The intermediacy of the 1,4-diradical is strongly supported by the isolation of 2-adamantyl-2'-phenylallyl sulfide 27 with the thietane 28 when α-methylstyrene is used as substrate (31 and 32). The thietane 28 is formed by the cyclization of the 1,4-diradical 26 while 2-adamantyl-2'-phenylallyl sulfide was produced by hydrogen abstraction via a six-membered ring transition state. In addition, as in oxetane formation (3) or enone addition (50) the diradical could also undergo fragmentation to the ground state starting materials (an exciplex preceding the genesis of the 1,4-diradical cannot be excluded (49)).



Scheme 1



Scheme 2

The partition function between the diradical (or exciplex) going on to product (thietane 17 in this case) or reversing to starting material was found (from the intercept of the plot in Figure 7) to be 1:580.

CHAPTER 4

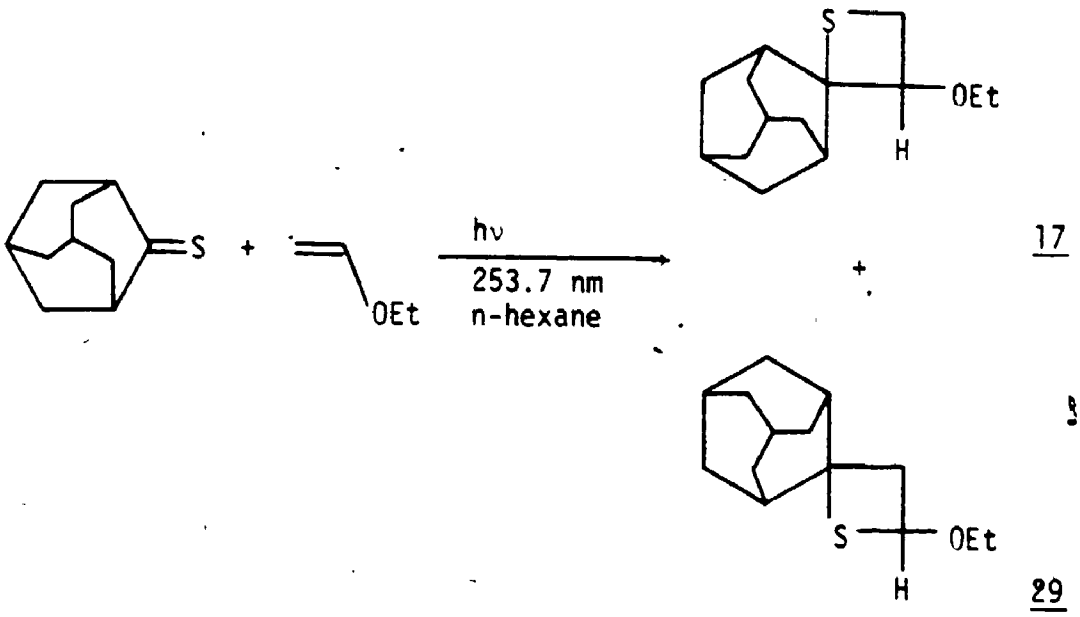
PHOTODIMERIZATION AND PHOTOCYCLOADDITION OF ADAMANTANETHIONE TO ETHYL VINYL ETHER AT 250 nm

4.1 Introduction

Liao and de Mayo have already reported (32) that irradiation of adamantanethione in n-pentane using light of 253.7 nm gives the dimer 16 as the major product, and that, in contrast to the dimerization induced by long wavelength irradiation (described in Chapter 3) the reaction was comparatively a rapid process. No kinetic study was undertaken at that time. Liao also reported (31) that irradiation of adamantanethione (253.7 nm) in the presence of ethyl vinyl ether gave no detectable amount of thietane 17 (by nmr analysis), even though the irradiation was carried out to the extent of 65% conversion (destruction of the thietane (15) or secondary photochemical attack of adamantanethione on the thietane (72) cannot be excluded). The reaction mixture was very complicated. We thus initiated the present work with the aim of clarifying the wavelength dependence phenomenon, characteristic of adamantanethione.

4.2 Addition of Adamantanethione to Ethyl Vinyl Ether

In contrast to Liao's report, when a n-hexane solution of adamantanethione was irradiated (λ = 253.7 nm) in the presence of ethyl vinyl ether, two isomeric thietanes 17 and 29 were produced (among other products) in a ratio of ca. 1:2 respectively.



In this respect, although the photochemical addition of acetone to 1-methoxy-1-butene for example has been shown (9) to be non-regiospecific, all photochemical cycloaddition reactions of thiones to olefins published up to date are regiospecific (15-22) and the above reaction is the first example of non-regiospecificity encountered in the photocycloaddition of thiones to olefins (the formation of thietane 29 in trace amount in a reversible process upon irradiation at 500 nm cannot be excluded.

The minor component 17 was shown to be identical to an authentic sample prepared by Liao (irradiation of adamantanethione in the presence of ethyl vinyl ether; λexcitation >420 nm) by V.P.C. retention time, and by I.R. and nmr spectroscopy. The structure of thietane 29 was determined spectroscopically. The gross structure followed from its nmr spectrum (see Figure 11 and Table 4). It is interesting to note that the methylene protons of the ethoxy group (ABX_3 system) were magnetically non-equivalent. A similar

Figure 11. Nmr Spectrum of Thietane 29

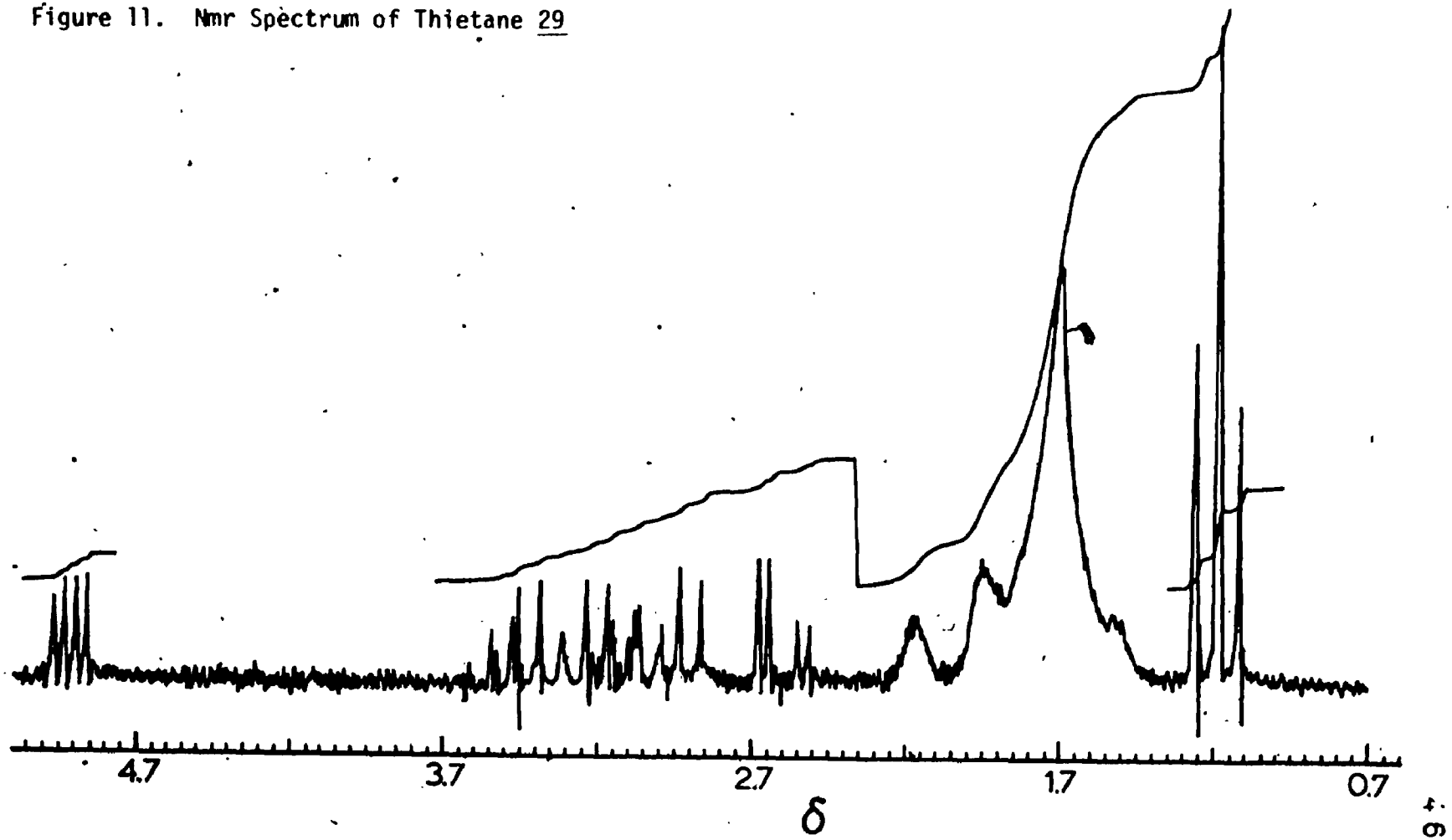
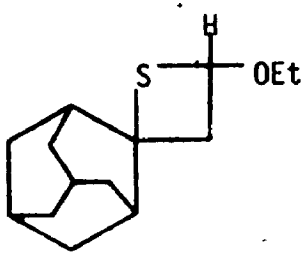
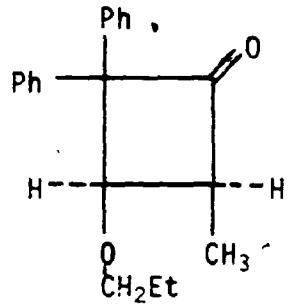


Table 4. NMR spectrum of thietane 29

Compound	Chemical Shift (δ)
 29	1.20 (3H, X_3 part of an ABX_3 system, $J_{AX} = J_{BX} =$ 7Hz, $OCH_2\underline{CH_3}$), 1.4 - 2.3 (14H, the protons on the adamantyl skeleton), 2.59 - 2.97 (2H, A part and B part of an ABX system respectively, $J_{AX} = 7.3$ Hz, $J_{BX} = 3.5$ Hz, $J_{AB} = 13$ Hz, $-\underline{CH_2}$-CHOEt), 3.10 - 3.45 (2H, AB part of an ABX_3 system, $J_{AB} = 9$ Hz, $O-\underline{CH_2}CH_3$), 4.92 (1H, X part of an ABX system, $J_{AX} = 7.3$ Hz, $J_{BX} = 3.5$ Hz).

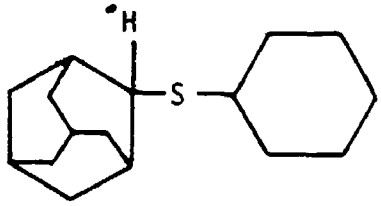
phenomenon of the magnetic non-equivalence of methylene protons has also been observed in the thietane 17 by Liao (31) and in compound 30 by Huisgen et al (73) (the ethyl group is either directly attached



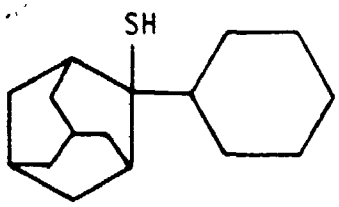
30

to an asymmetric centre or separated by one atom from it). The disposition of the ethoxy group on the thietane ring was deduced from its mass spectrum. The mass spectrum showed the expected molecular ion peak at m/e 238. The presence of the fragment at m/e 148 due to M-SCHOEt ion and the absence of the peak at m/e 192 due to M-CH_2S species allowed the unequivocal assignment of structure 29 to this thietane. In contrast, the mass spectrum of thietane 17 showed the presence of the m/e 192 peak and the absence of the m/e 148 fragment (31).

The complex mixture obtained upon irradiation of adamantanethione at short wavelength seemed to contain products originating from the interaction of the thione with the solvent. In fact, irradiation of adamantanethione in cyclohexane at 253.7 nm gave 2-cyclohexylthioadamantane 31 and the thiol 32.

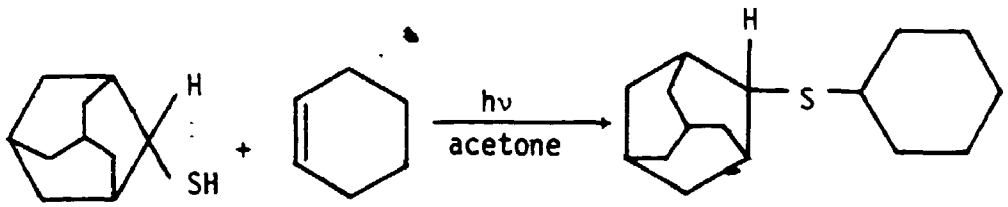


31



32

Compound 31 was prepared independently by irradiating an acetone solution of 2-adamantylthiol and cyclohexene (74).



31

The structure of 31 was determined spectroscopically. The mass spectrum showed the expected molecular ion peak at m/e 250 and the fragment at m/e 135 due to the $M-SC_6H_{11}$ ion. In contrast, the mass spectrum of 32 showed a much less intense molecular ion peak at m/e 250 (compared to 31) and a pronounced peak at m/e 216 due to the $M-H_2S$ ion. Furthermore the nmr spectrum of 32 shows a sharp singlet at 1.2 ppm due to the thiol hydrogen.

Irradiation of a cyclohexane solution of adamantanethione in the n,π^* absorption band (λ= 500 nm) yielded no trace of 31 or 32 (glpc analysis) providing preliminary indication that the reactive species at short wavelength (responsible for the formation of 31 and

32) is not the lowest n,π* triplet state of adamantanethione.

4.3 Quantum Efficiencies for Dimer Formation

When a n-hexane solution of adamantanethione (6.46×10^{-3} M) was irradiated at 250 nm (whereas at 500 nm, the choice of benzene as solvent was dictated by relative solubility problems for quenching and sensitization studies, the use of benzene as solvent at 250 nm was precluded by absorption problems), the quantum yield for dimer 16 formation was found to be 2.8×10^{-2}, i.e. the quantum yield of dimerization is 200 times larger than that measured following irradiation at 500 nm of a benzene solution of the thione (0.2 M) (see Chapter 3). The difference in extinction coefficient of over three orders of magnitude at the two wavelengths (see Figure 1) precluded the use of the same concentrations of the thione. The reaction at short wavelength may therefore well be from a different excited state, but must be going to some extent from at least two pathways. The decay of S_2 is, presumably partly to S_1. The latter will intersystem cross with unit efficiency to T_1 (see Chapter 3) in the same manner as if generated directly. However, since the quantum yield of dimer from T_1 derived from S_1 is of the order of 0.5% of that from S_2, the contribution will be very small.

The concentration of adamantanethione (6.46×10^{-3} M), excludes the possibility that the dimer obtained by excitation at 250 nm derives from the second excited singlet state (S_2) since this would imply an exceptionally long lifetime ($\sim 10^{-8}$ sec) for the S_2 state of adamantanethione (we make here the explicit assumption that trapping of the S_2 state by thione is diffusion-controlled, hence

$\tau^{-1}(S_2) \approx 10^{10}\ M^{-1}\ sec^{-1} \times 6.46 \times 10^{-3}\ M \approx 10^{8}\ sec^{-1}$), furthermore, at least 50% of the dimer formation can be quenched with 1,1'-azoisobutane giving a linear Stern-Volmer plot (see Figure 12 and Table 5) and the quenching efficiency compares well with the quenching of adamantanethione triplet at 530 nm with the same quencher. It would therefore appear that dimerization (at 6.46×10^{-3} M) occurs via a long-lived species (tentatively assigned as the lowest triplet state of adamantanethione (63)) which can be efficiently trapped by ground state thione molecules or transfer energy to an external quencher (the low efficiency of dimer formation at 500 nm compared to 250 nm was attributed to an energy wasting process involving quenching of the S_1 state of adamantanethione by ground state molecules).

The low-conversion ($\sim$ 1%) quantum yield of dimerization as a function of the concentration of adamantanethione was then studied. The results of these measurements are presented in Table 6 and Figure 13. Figure 13 indicates that plots of $1/\Phi_{Dim}$ vs. $1/[C{=}S]$ give a reasonable straight line up to the concentration of 0.04 M. The curvature observed at higher concentrations ($\sim$0.07 M) provides evidence for the complexity of the dimerization mechanism and may be due to direct excitation of ground state aggregates according to the following scheme

$$S_o + S_o \rightleftharpoons S_{o_2}$$

$$S_{o_2} \xrightarrow{h\nu} S_{o_2}^*$$

$$S_{o_2}^* \longrightarrow \text{dimer}$$

$\tau^{-1}(S_2) \simeq 10^{10}\ M^{-1}\ sec^{-1} \times 6.46 \times 10^{-3}\ M \simeq 10^{8}\ sec^{-1}$), furthermore, at least 50% of the dimer formation can be quenched with 1,1'-azoisobutane giving a linear Stern-Volmer plot (see Figure 12 and Table 5) and the quenching efficiency compares well with the quenching of adamantanethione triplet at 530 nm with the same quencher. It would therefore appear that dimerization (at 6.46×10^{-3} M) occurs via a long-lived species (tentatively assigned as the lowest triplet state of adamantanethione (63)) which can be efficiently trapped by ground state thione molecules or transfer energy to an external quencher (the low efficiency of dimer formation at 500 nm compared to 250 nm was attributed to an energy wasting process involving quenching of the S_1 state of adamantanethione by ground state molecules).

The low-conversion ($\sim 1\%$) quantum yield of dimerization as a function of the concentration of adamantanethione was then studied. The results of these measurements are presented in Table 6 and Figure 13. Figure 13 indicates that plots of $1/\Phi_{Dim}$ vs. $1/[C{=}S]$ give a reasonable straight line up to the concentration of 0.04 M. The curvature observed at higher concentrations ($\sim$0.07 M) provides evidence for the complexity of the dimerization mechanism and may be due to direct excitation of ground state aggregates according to the following scheme

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$$S_{o_2} \xrightarrow{h\nu} S_{o_2}^*$$

$$S_{o_2}^* \longrightarrow \text{dimer}$$

$$S_{o_2}^{*} \longrightarrow S_o + S_o$$

where S_{o_2} represents a ground state association (association limited to the dimer stage has been assumed for simplicity) and $S_{o_2}^{*}$ represents an excited molecular associate (i.e., an excimer) which could proceed on to dimer or decay back to two adamantanethione ground state molecules. Kleopfer and Morrison (75) studied the photodimerization of dimethylthymine in 0.1 M aqueous solution and provided evidence for a mechanism involving direct excitation of ground state aggregates.

The possibility of ground state association mentioned above, led us to test the validity of Beer's Law in different solvents. The results of these measurements presented in Table 7 and Figures 14 and 15 provide ample confirmation for such ground state aggregation at least in n-hexane. Whereas at 263.5 and 465 nm the absorption of adamantanethione in n-hexane obeys Beer's Law over a concentration range of three powers of ten (see Figure 14), at 275 nm however, the increase in the absorption is not linear with the concentration (see Figure 15). A rationale for this is aggregate formation and that the associated species absorbs in the 275 nm region. A similar ground state aggregation has been reported by Blackwell et al (42) in the case of Michler's thione. In acetonitrile, however, the increase in the optical density was linear within the concentration range studied (the concentration limit (0.2 M) was dictated by solubility problems), implying inefficient ground state association in polar solvents.

It was necessary therefore to study the effect of solvent on the photochemical behaviour of adamantanethione. The results

Table 5. Quenching of Dimer Formation at 250 nm by 1,1'-Azoisobutane

Quencher (M)	Φ_o/Φ_Q	Φ_Q^{-1}
0.023	1.13	39.78
0.088	1.25	44.0
0.132	1.39	48.9
0.199	1.74	61.2

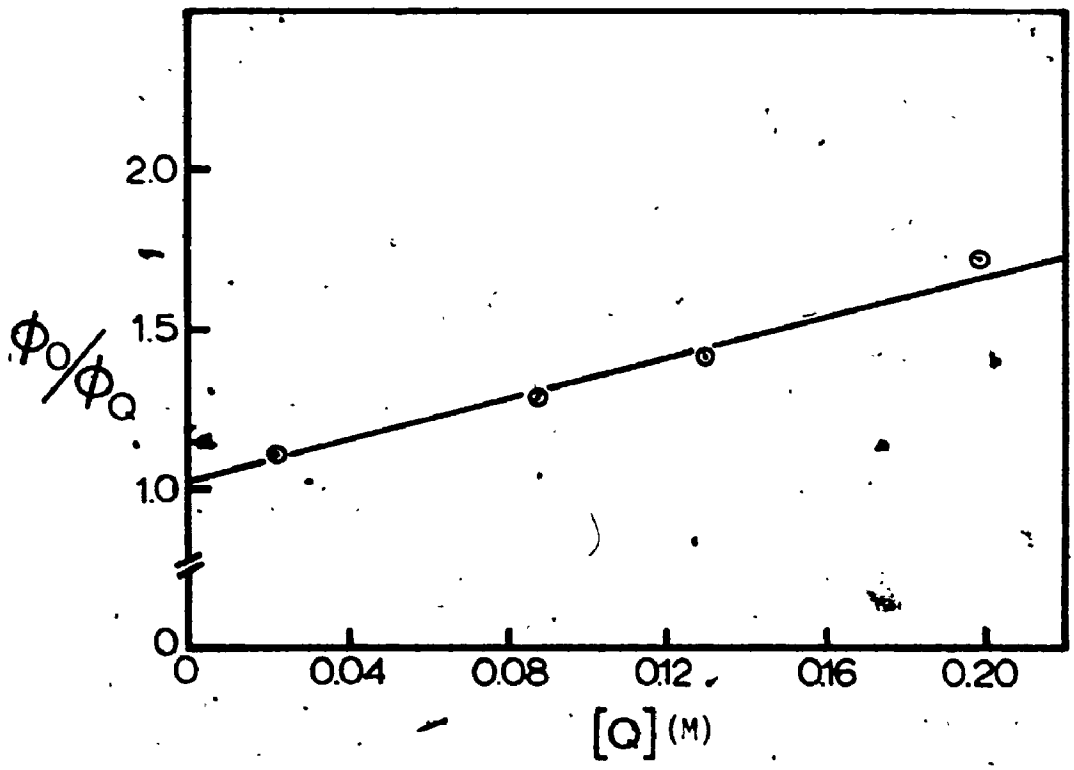


Figure 12. Stern-Volmer Plot of the Quenching of Dimer 16 Formation at 250 nm with 1,1'-Azoisobutane.

Table 6. The Concentration Effect of Adamantanethione on the Quantum Yield of Dimerization at 250 nm

Concentration (M)	Φ_{Dim}	Φ_{Dim}^{-1}
0.00608	0.0266	37.5
0.00646	0.0284	35.21
0.010	0.0349	28.6
0.0207	0.0410	24.36
0.0282	0.0435	22.98
0.040	0.0461	21.66
0.0689	0.0581	17.20
0.0854	0.0638	15.66
0.200	0.138	7.20

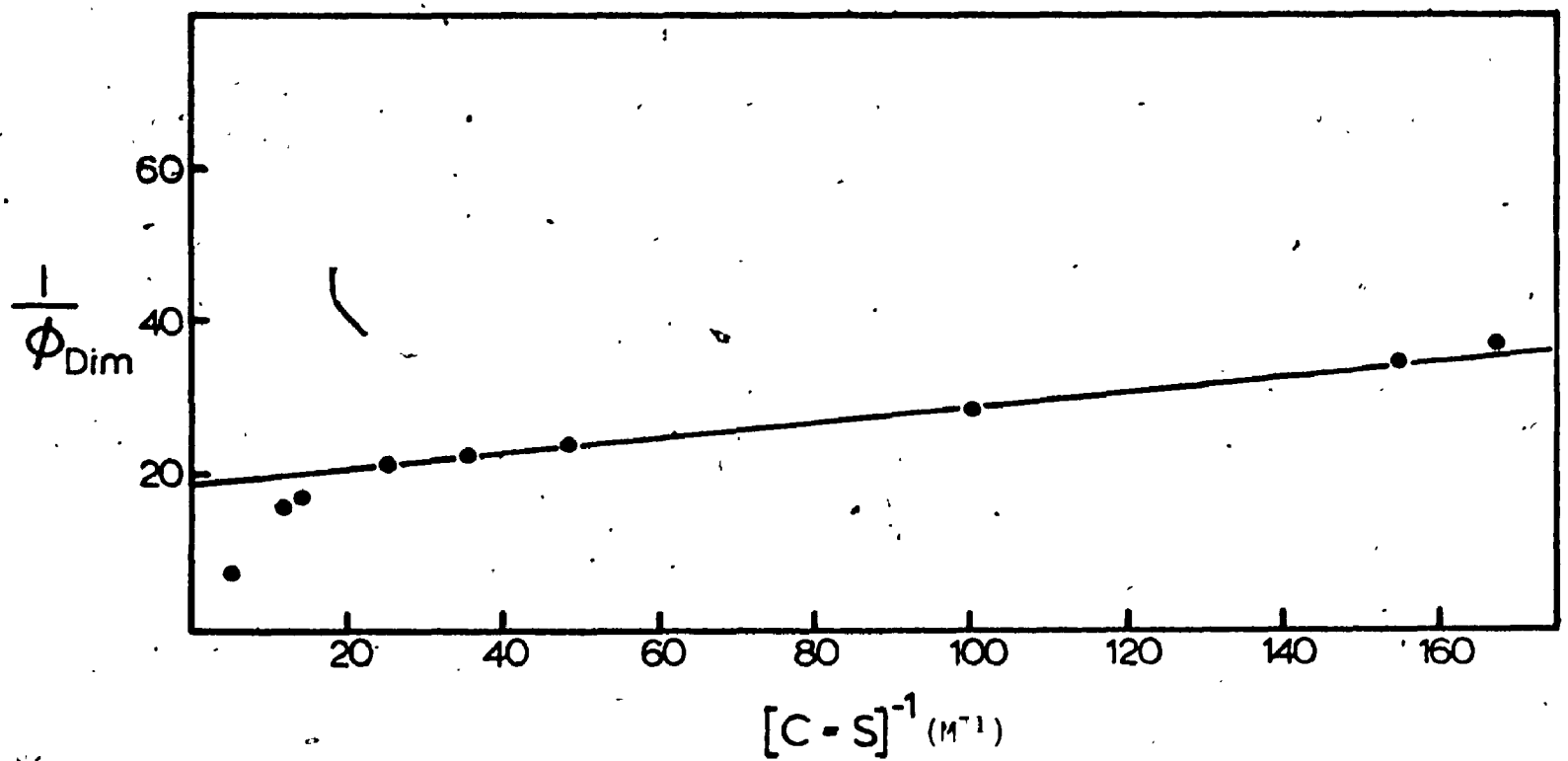


Figure 13. Quantum Yield of Dimerization at 250 nm as a Function of Adamantanethione Concentration.

Table 7. Variation of the O.D. of Adamantanethione with Concentration and Wavelength

Concentration (M)	Optical Density			
	n-hexane			acetonitrile
	λ=263.5nm+	λ=275nm+	λ=465nmØ	λ=285nm*
0.30	-	0.306	1.60	-
0.20	2.599	0.179	1.14	0.77
0.15	1.944	0.123	0.80	0.50
0.10	1.310	0.077	0.598	0.381
0.075	0.989	0.058	0.410	0.26
0.0375	0.494	0.028	0.199	0.128
0.0075	0.098	0.055*	0.038	0.025

\+ path length 0.01 cm

* path length 0.1 cm

Ø path length 1.0 cm

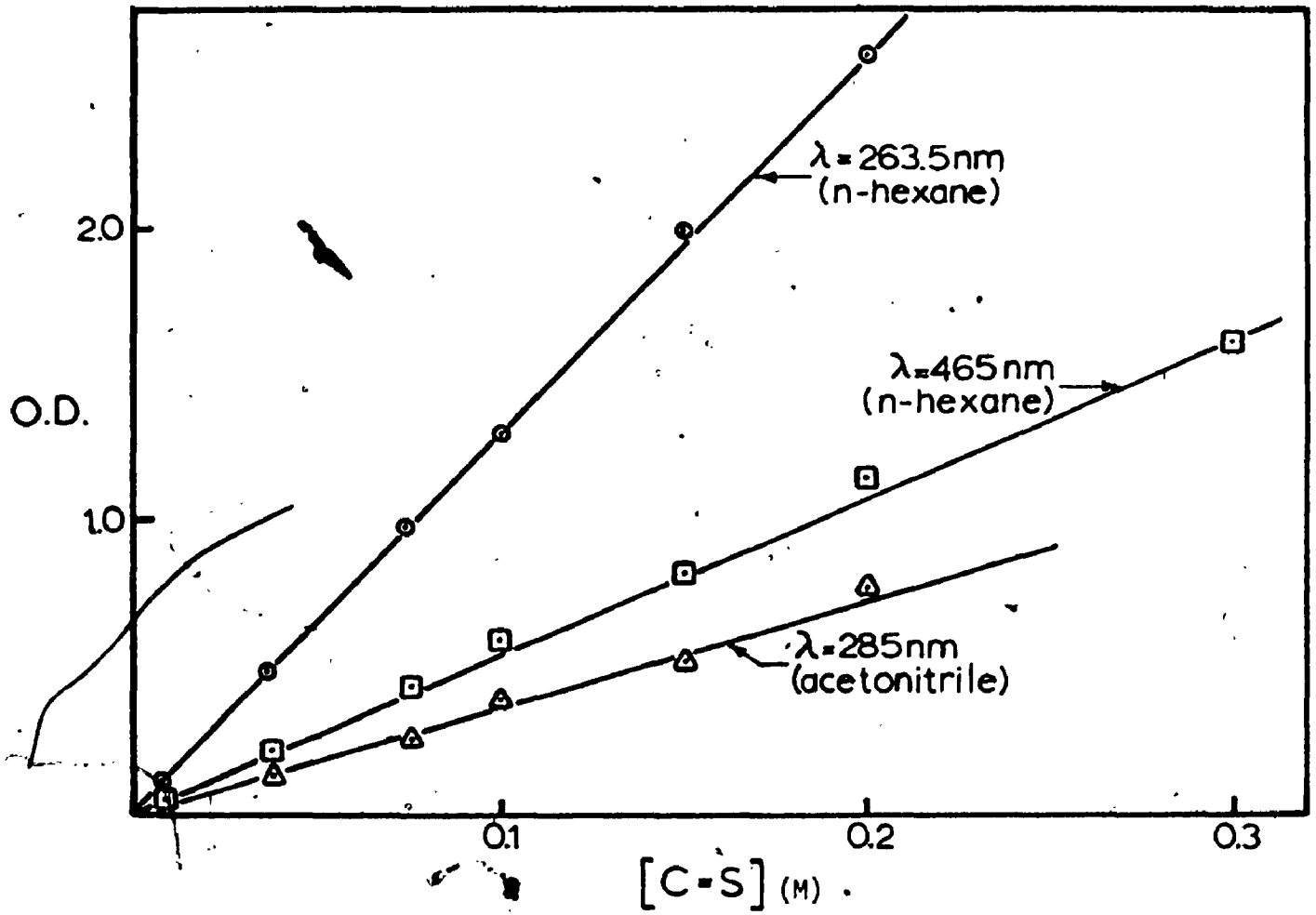


Figure 14. Variation of the O.D. of Adamantanethione with Concentration at 263.5, 465 and 285 nm.

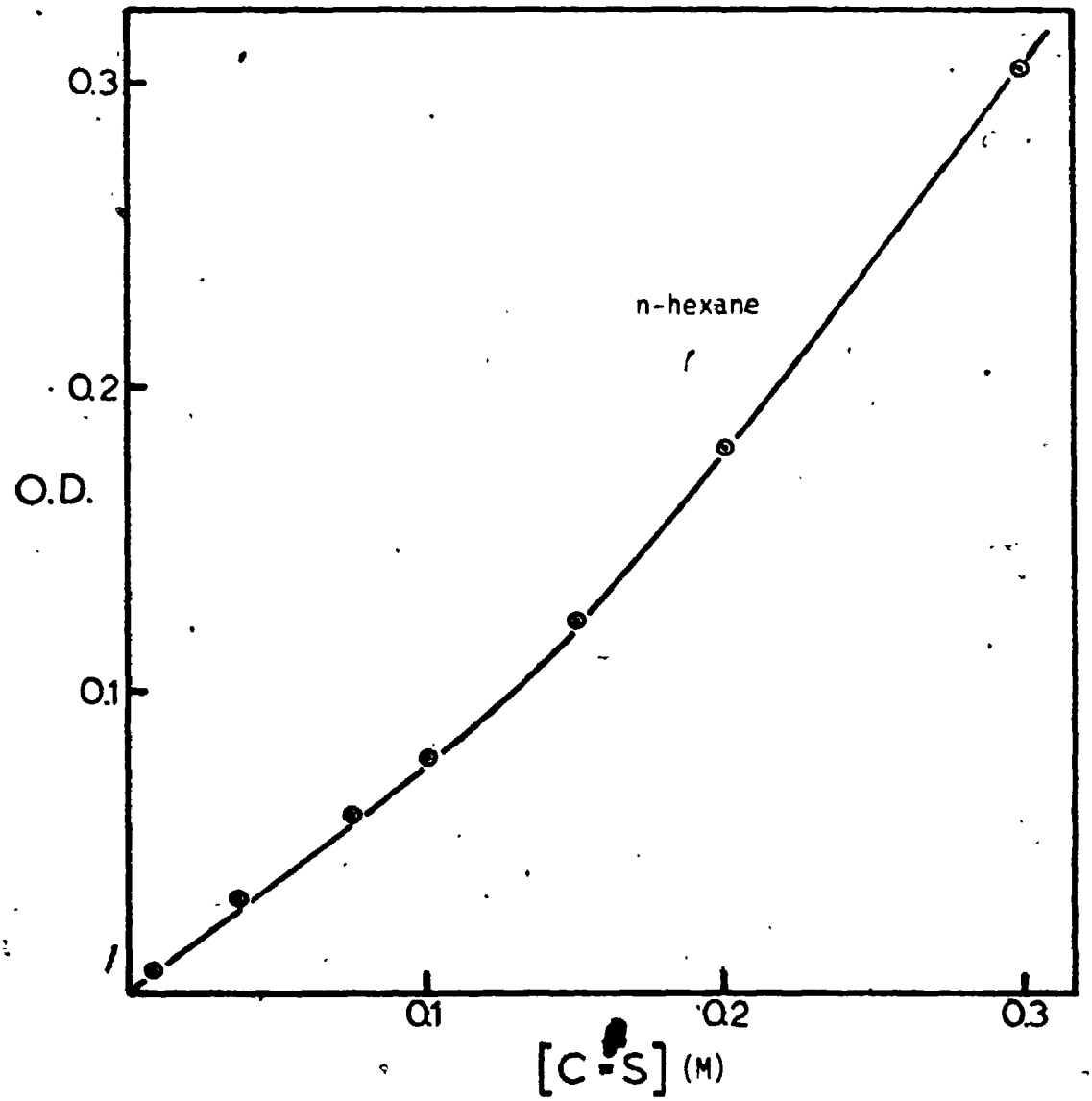
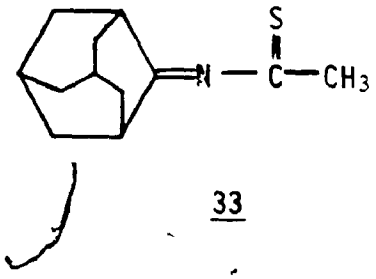


Figure 15. Variation of the O.D. of Adamantanethione with Concentration at 275 nm.

shown in Figures 16 and 17 clearly indicate that the photochemistry of adamantanethione at 250 nm (in contrast to 500 nm) varies strongly with solvent polarity (the thione is consumed faster in non-polar solvents) and that the reactive species at short wavelength is not the lowest triplet. In acetonitrile, the observed increase in the optical density with time in the 430-450 nm region (see Figure 17) is presumably due to the formation of an addition product 33 (detected by tlc) between adamantanethione and acetonitrile.



33

Our conclusion is based on the observation made by Blackwell et al (76) (photochemical formation of the N-thioacylketimine function).

It was also found that whereas the quantum yield of dimer formation for a n-hexane solution of adamantanethione (6.46×10^{-3} M) is 2.8×10^{-2}, for the same concentration in acetonitrile, Φ_{Dim} was estimated to be $<10^{-4}$. For a n-hexane solution of the thione (0.2 M), Φ_{Dim} was found to be the same within experimental error ($\Phi_{Dim} = 0.13$) whether excitation was conducted at 250 or 278 nm.

In summary, the foregoing results clearly demonstrate the complexity of the mechanism of photodimerization of adamantanethione at 250 nm and we are thus left with the postulate that at high concentration of the thione, ground state aggregation occurs in non-

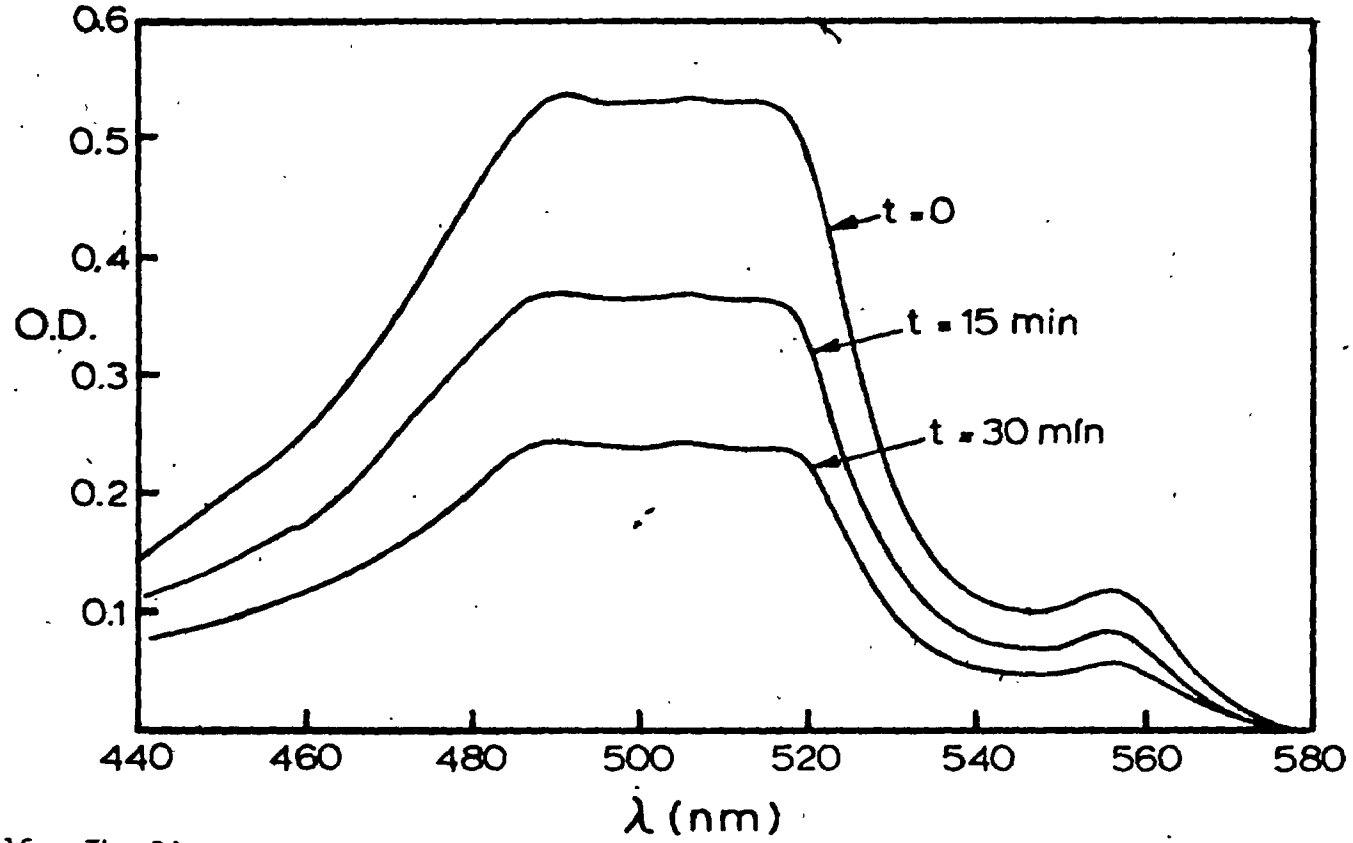


Figure 16. The Disappearance of Adamantanethione (Cyclohexane).

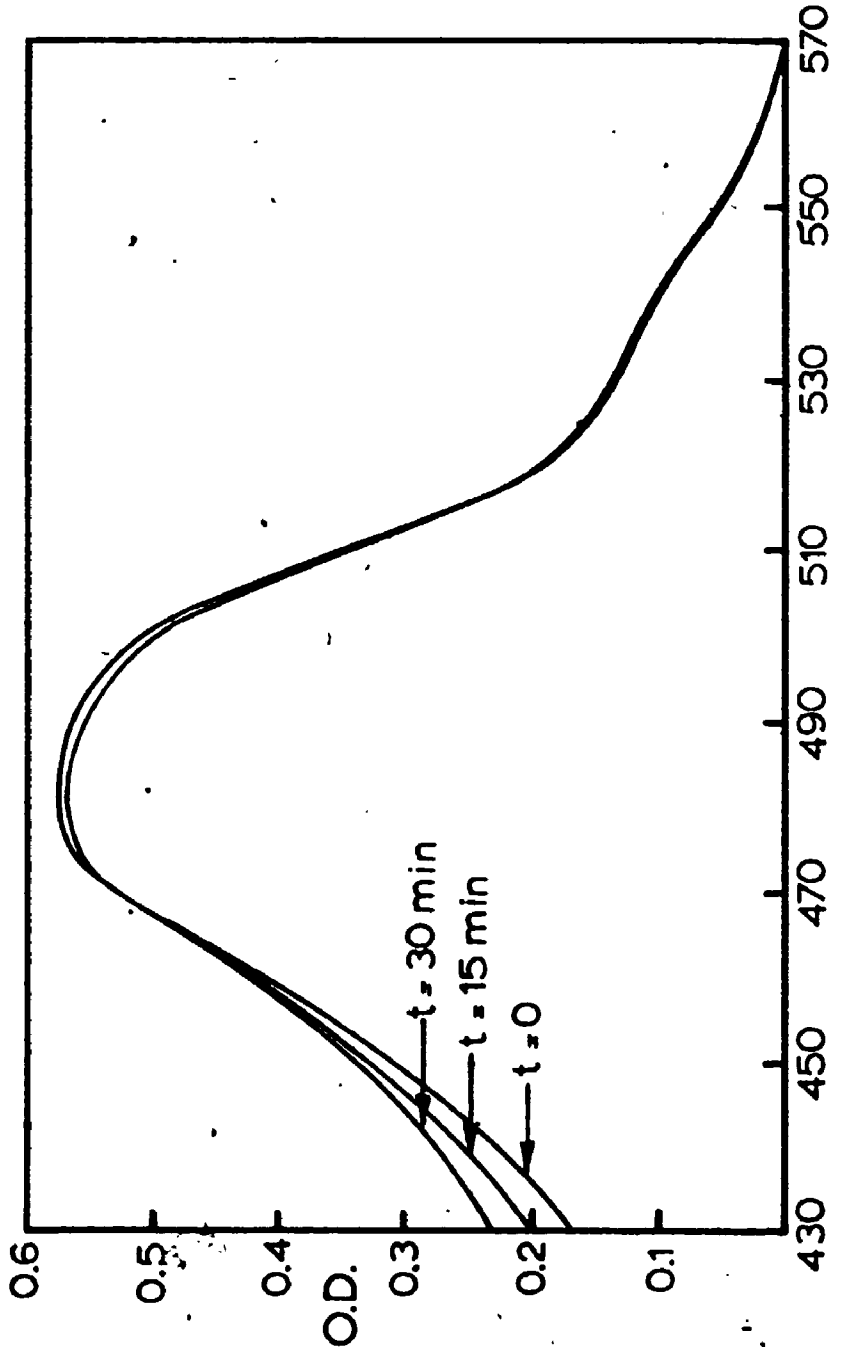


Figure 17. The Disappearance of Adamantanethione (Acetonitrile).

polar solvents and is partially responsible for dimerization. At low concentration however, the mechanism is still obscure and efforts are required to identify the nature of the long-lived species quenched by 1,1'-azoisobutane.

4.4 Mechanistic Investigations of the Photocycloaddition of Adamantanethione to Ethyl Vinyl Ether

While irradiation of a benzene solution of adamantanethione at 500 nm in the presence of ethyl vinyl ether yields essentially thietane 17 ($\phi = 4.6 \times 10^{-4}$; 0.2 M thione and 2.0 M olefin), short wavelength irradiation ($\lambda = 250$ nm) of a n-hexane solution of the same mixture gives two isomeric thietanes 17 and 29 among other products (see above). The quantum yield for thietane 17 formation was found to be 1.6×10^{-2} i.e., ~35 times larger than that measured following irradiation at 500 nm.

Similar to the photodimerization, the formation of the thietane 17 is quenched by the addition of increasing concentrations of 1,1'-azoisobutane (see Figure 18 and Table 8).

The ratio of isomeric thietanes 29 to 17 was then determined as a function of the percentage conversion of adamantanethione. The results shown in Figure 19 indicate a constant value throughout the conversion limit investigated (2.0 - 50.1%).

Whereas the photodimerization of adamantanethione at 250 nm could be partly explained by the excitation of a ground state association (this was supported by spectroscopic evidence and by the strong dependence of the quantum yield of dimerization on the dielectric constant of the medium), for the photocycloaddition

Table 8. Quenching of Thietane 17 formation at 250 nm by 1,1'-azoisobutane

Quencher (M)	Φ_o/Φ_Q	Φ_Q^{-1}
0.10	1.20	136.36
0.20	1.45	164.77
0.30	1.70	193.18
0.45	2.05	232.95

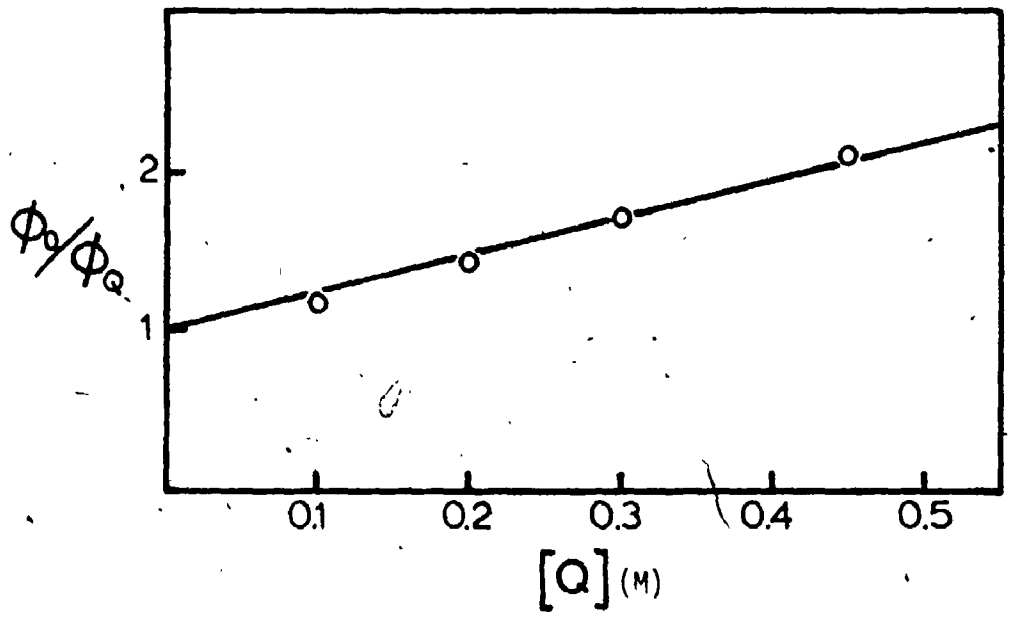


Figure 18. Stern-Volmer Plot of the Quenching of Thietane 17 Formation at 250 nm with 1,1'-Azoisobutane.

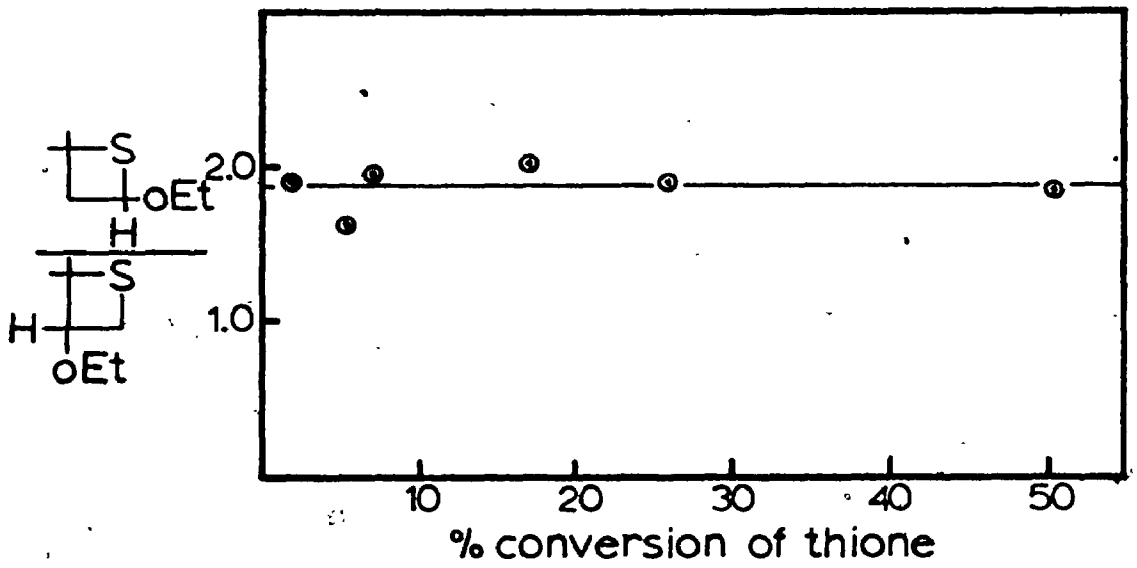


Figure 19. The Ratio of Isomeric Thietanes as a Function of the Percentage Conversion of Adamantanethione.

reaction, we have no direct method for excluding the possibility of a ground state association between adamantanethione and ethyl vinyl ether. However, it appears that such association (as in the case of photodimerization), would be dependent on solvent polarity. But it was found that the regioselectivity ratio 29/17, which reflects the direction of attack of the excited species from adamantanethione on ethyl vinyl ether or reflects the orientation of the ground state association is constant (~2.0) whether cyclohexane or acetonitrile was used as the solvent (after 17% conversion of the thione). Furthermore the quantum yield of thietane 17 formation in acetonitrile (at 0.2 M thione and 2.0 M olefin) was equal within experimental error to that obtained in n-hexane. The above mentioned results do not support direct excitation of a performed ground state association between the thione and ethyl vinyl ether, and the following questions still remain: (a) what is the nature and multiplicity of the reactive species responsible for photocycloaddition? (b) is more than one intermediate involved and what is the chemical nature of the intermediate(s)?.

CHAPTER 5

PHOTOREDUCTION OF ADAMANTANETHIONE WITH 2-ADAMANTYLTHIOL

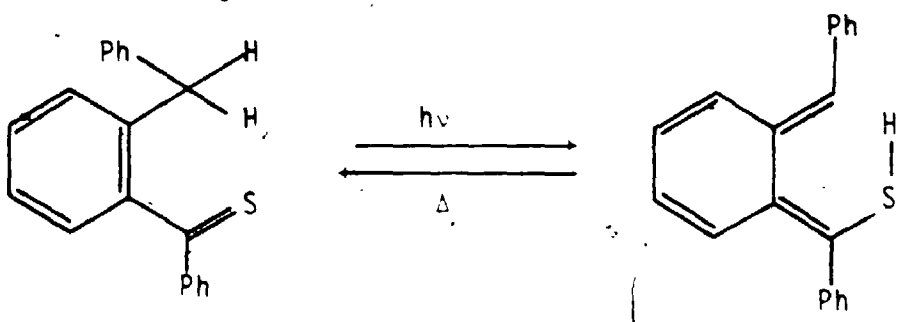
5.1 Introduction

While the photoreduction of carbonyl compounds, yielding mainly pinacols and the corresponding alcohols, has been of interest to photochemists (1, 4, 77, 78 and 79) and spectroscopists (34, 80, 81 and 82) for many years, in contrast, the photoreduction of the thiocarbonyl group has been reported in few instances and concerns the aromatic thiocarbonyl compounds only. Oster (13) reported that thiobenzophenone is photoreduced in ethanol to give the thiol 34, disulfide 35, and tetrasulfide 36. The corresponding thiopinacol was not observed. He was also the first to report that the photoreduction

$$Ph_2C{=}S \xrightarrow[h\nu \\ 366\ nm]{EtOH} \underset{\underline{34}}{Ph_2CHSH} + \underset{\underline{35}}{Ph_2CH\text{-}S\text{-}S\text{-}CHPh_2} + \underset{\underline{36}}{Ph_2CH\text{-}S\text{-}S\text{-}CPh_2\text{-}S\text{-}S\text{-}CHPh_2}$$

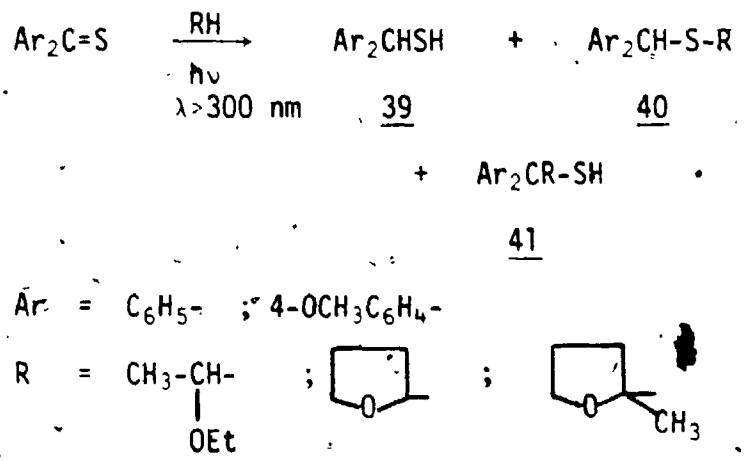
of thiobenzophenone is wavelength dependent, observing that the reaction did not occur at 588 nm, but yielded the above mentioned products when 366 nm light was used.

Kito and Ohno (14) were able to trap the photoenethiol 38 of o-benzylthiobenzophenone 37 by irradiation in deuterated methanol. They also reported (83) the photochemical reactions of thiobenzophenone



37 38

and 4,4'-dimethoxythiobenzophenone with diethyl ether, tetrahydrofuran and 2-methyltetrahydrofuran. The products obtained upon irradiation with light >300 nm are the corresponding thiol 39, the sulfide 40 and the thiol 41. They found that the reactions involve stable transient



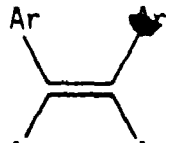
free radicals of the type Ar_2C-SR, identified by esr spectroscopy (g = 2.0051; Ar = C_6H_5). They proposed a chain mechanism for the reaction (initial hydrogen abstraction taking place by the n,π* triplet of the thione), although no evidence was provided for such conclusions.

Loutfy (84 and 85) investigated the photoreduction of

Michler's thione by the corresponding thiol and found that the main product was the disulfide 42, accompanied by p,p'-Bis(dimethylamino) biphenyl 43 and the olefin 44. The latter two products were formed upon irradiation of Michler's thione in benzene in the absence of the thiol. He did not study the mechanism.

$$Ar_2C{=}S + Ar_2CHSH \xrightarrow[\text{benzene}\ \lambda>400\ nm]{h\nu} Ar_2CH\text{-}S\text{-}S\text{-}CHAr_2$$

42

+ Ar - Ar + 

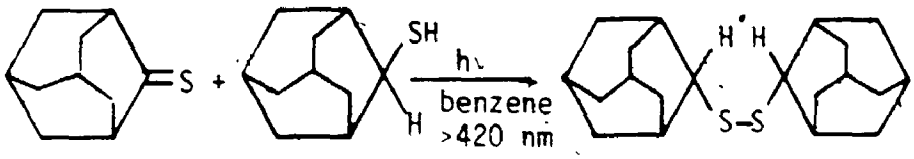
43 44

Ar = $4\text{-}Me_2NC_6H_4$-

It has been found that adamantanethione undergoes photoreduction in the presence of isopropyl alcohol or alkylbenzenes (toluene and isopropylbenzene) to give a complicated mixture (86). This led us to reinvestigate the photoreduction of adamantanethione, simplifying the system by using the corresponding thiol as the hydrogen donor, with the hope that the investigation of the reaction would not involve characterization of complex mixtures of products.

5.2 Product and Mechanistic Investigations

Irradiation of a benzene solution of adamantanethione (λ>420 nm) in the presence of 2-adamantylthiol gave, in a clean reaction, the disulfide 45 as the sole product.



45

The structure of this compound was deduced from its spectroscopic properties. The ultraviolet spectrum showed absorption at 250 nm (ε= 400) (87 and 88) (see Figure 20). The mass spectrum exhibited the diagnostic peaks at m/e 334 (molecular ion peak), 167 ($C_{10}H_{15}S$) and 135 ($C_{10}H_{15}$, adamantyl group). The nmr spectrum (see Experimental) confirmed this assignment as well. Finally, the structure was substantiated by independent synthesis of 2-adamantyldisulfide 45 from 2-adamantylthiol by ferric chloride oxidation.

Three approaches were made to provide unequivocal evidence for the chemical mechanism of the reaction. The first consisted of a quantum yield study of the photoreduction of adamantanethione with 2-adamantylthiol. Irradiation was carried out at 468 nm and the disappearance of the thione was followed by monitoring its absorption at 500 nm.

When a benzene solution of adamantanethione (6.12×10^{-2} M) and 2-adamantylthiol (7.28×10^{-1} M) was used, the quantum yield of adamantanethione disappearance (10.71% conversion) was found to be 1.77. In a duplicate experiment, the quantum yield (12.52% conversion) was found to be 2.10, i.e. greater than unity; indicating a chain reaction (a blank experiment established that the reaction

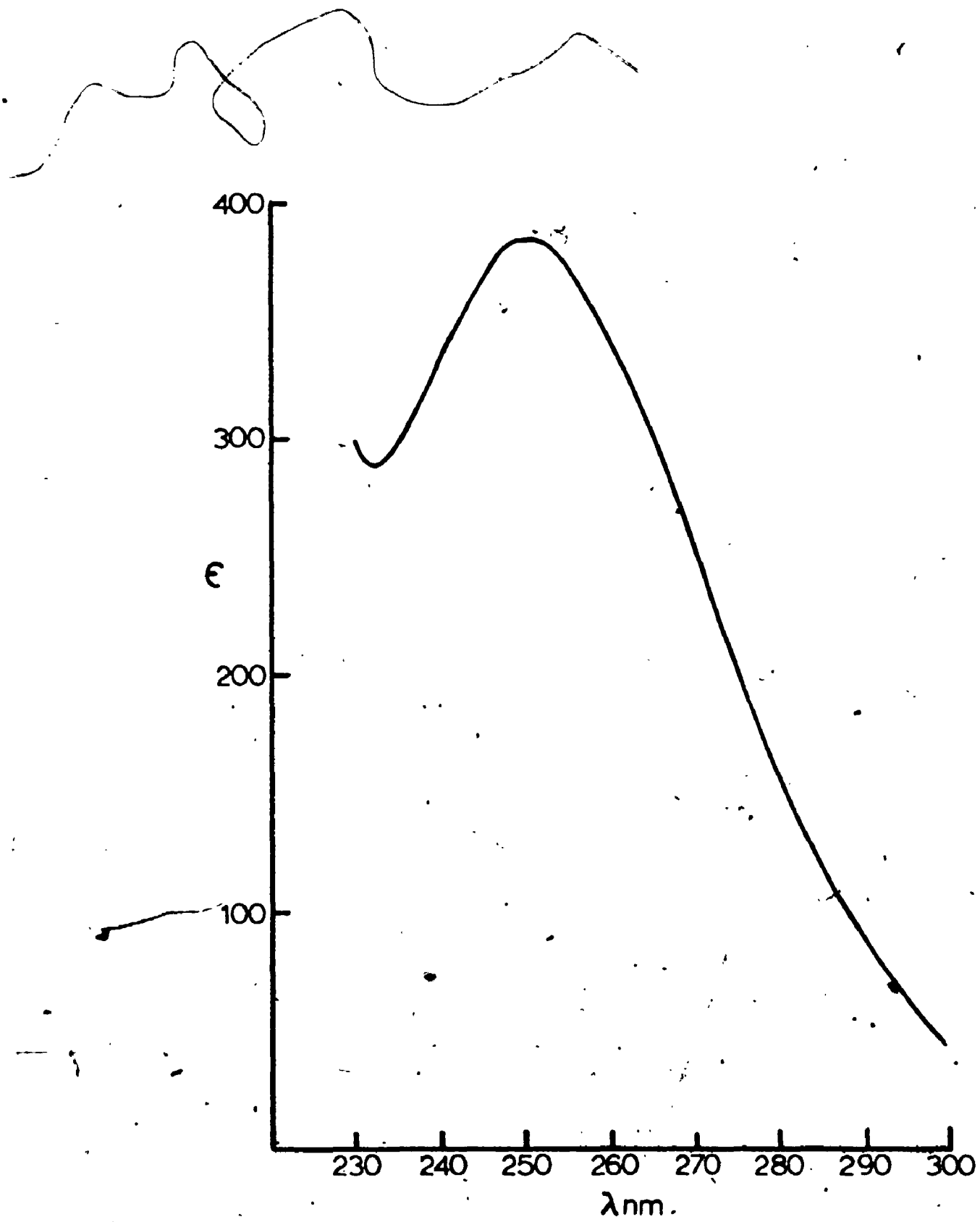


Figure 20. The Absorption Spectrum of 2-Adamantyldisulfide in n-hexane.

is initiated by light).

On the basis of the above information, a mechanism is proposed (see Scheme 3) for the production of disulfide 45 from adamantanethione and 2-adamantylthiol. The reaction is written as a chain process, but the quantum yield observed is a function of several factors including chain length. The nature of the termination step is not known, but if it be the coupling of two thyil radicals the chain length must be long. Coupling of two thioketyl radicals 46, as another termination process can be excluded since no thiopinacol was formed.

The nature of the propagation step involving trapping of the thyil radical by a ground state molecule of adamantanethione illustrates the extremely efficient radical scavenging character of thioketones (89). The initiation step can be rationalized as follows: the excited state produced by the $n\rightarrow\pi^*$ transion of adamantanethione undergoes quantitative intersystem crossing (see Chapter 3) with the production of the long-lived n,π^* triplet. The latter is, therefore, the chemically reactive species abstracting hydrogen by its electrophilic half vacant n orbital (14).

Further support as to the validity of the mechanism proposed in Scheme 3 is provided by the following deuterium label experiment. A benzene solution of adamantanethione was irradiated (λ>420 nm; 8.36% conversion of the thione) in the presence of 2-deuterio-2'-adamantylthiol 49. The disulfide was again obtained and was analyzed by mass spectrometry for deuterium content. The results (see Experimental) indicate that the yield ratio of the di, mono and non-

Initiation

$$AdC{=}S + AdCHSH \xrightarrow[\text{benzene}\\ >420\ nm]{h\nu} AdC{-}SH + AdCHS\cdot$$

46 47

Propagation

$$AdCHS\cdot + AdC{=}S \longrightarrow AdCH{-}S{-}S{-}CAd$$

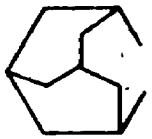
48

$$AdCH{-}S{-}S{-}CAd + AdCHSH \longrightarrow AdCH{-}S{-}CHAd + AdCHS\cdot$$

$$AdC{-}SH + AdCHSH \longrightarrow AdCHSH + AdCHS\cdot$$

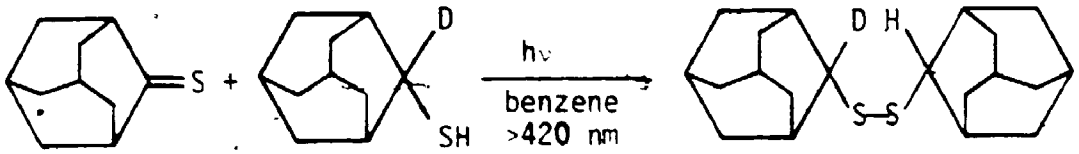
Termination

$$2\ AdCHS\cdot \longrightarrow AdCH{-}S{-}S{-}CHAd$$

Ad = 

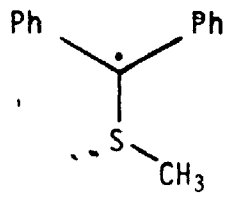
Scheme 3

deuterated disulfides is 0.02:1:0.05 respectively, i.e. the sample is principally monodeuterated. (If scheme 3 is operating, the resulting disulfide would essentially contain one deuterium only).

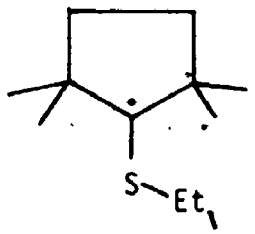


49 50

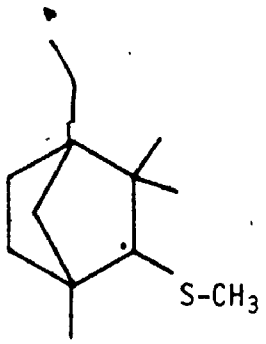
Further evidence as to the nature of the reactive intermediates is given from a study of esr spectra.* When a degassed n-pentane-ether solution of adamantanethione (0.22 M) and 2-adamantylthiol (1.1 M) was irradiated with light (>420 nm) in a cavity of an esr spectrometer at -170°C, a signal was observed (see Figure 21), g = 2.003 consistent with a carbon-centre radical (90 and 91) (higher g values are obtained for radicals where the electron is localized on sulfur; for liquid sulfur g = 2.024 (92). Attempts to



g = 2.0032 (90)



g = 2.0032 (91)



g = 2.0030 (91)

* The esr spectra were carried out by courtesy of Dr. J. R. Bolton.

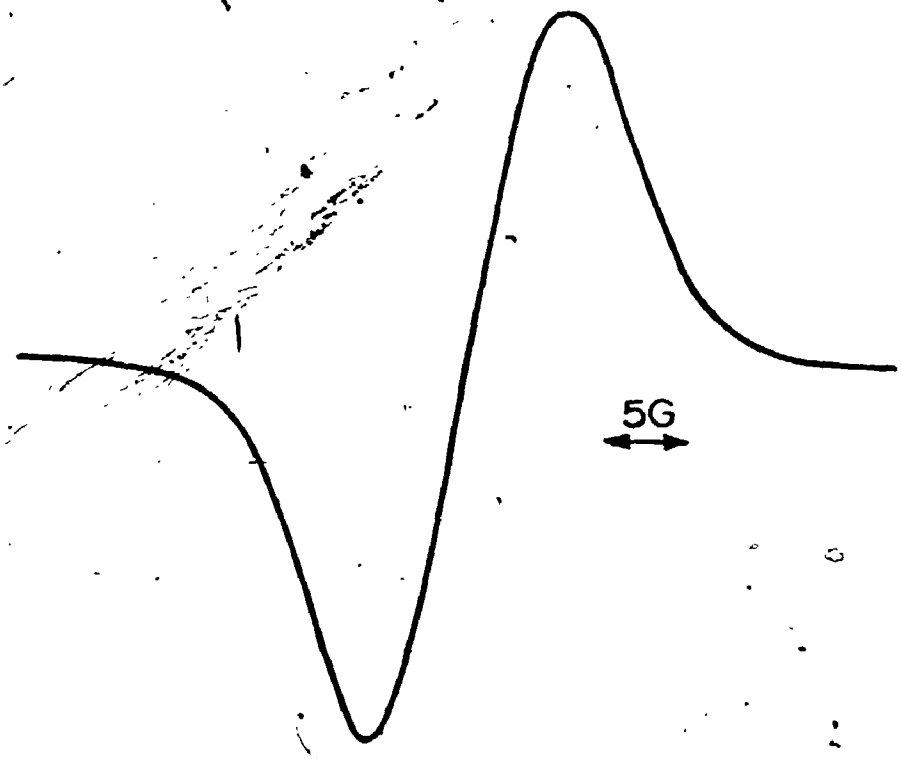


Figure 21. ESR Spectrum of Adamantanethione-2-Adamantylthiol System at -170°C, (g = 2.003).

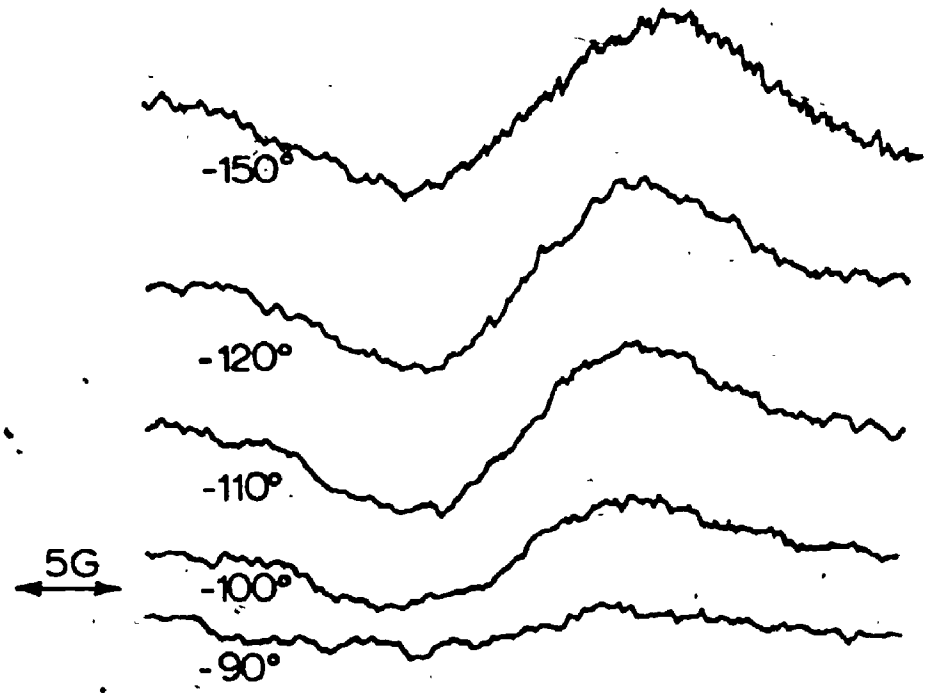


Figure 22. Effect of Temperature on ESR Spectrum of Adamantanethione-2-Adamantylthiol System.

detect hyperfine splitting by increasing the temperature failed and led to the disappearance of the signal at -90°C indicating a short lifetime for the intermediate radical. The subject is under further investigation by Dr. K. S. Chen.

In summary, both the production of disulfide 46, with quantum yield greater than unity and the results from the deuterium label experiment indicate that Scheme 3 is operating, in the irradiation of adamantanethione-2-adamantylthiol mixtures. The esr observations are also consistent with this scheme. The propogation step responsible for the chain nature of the reaction demonstrates the radical-trapping character of adamantanethione.

CHAPTER 6

EXPERIMENTAL

6.1 General Procedures

Melting points were taken on a Gallenkamp capillary melting point apparatus and are uncorrected. Infrared spectra (ir) were determined on Beckman IR-5A and IR-20A spectrophotometers. Ultraviolet spectra (uv) were measured on a Cary 14 spectrophotometer, unless otherwise stated. Neuclear magnetic resonance (nmr) spectra were recorded on Varian T-60 and HA-100 spectrometers with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported as δ values in parts per million (ppm) from TMS (δ = 0.00), while the coupling constants (J) are given in cycles per second (Hz). Mass spectra were run on a Varian M-66 spectrometer using polyfluoroalkane as calibrant; m/e values are given for the molecular ion peak and for other major peaks in the spectra. Rate constants were calculated using a least squares computer program. The solutions were degassed by freeze-thaw method (three cycles, 5 x 10^{-5} mm Hg).

6.2 Chemicals

Adamantanethione and 2-adamantylthiol were prepared according to the method of Greidanus (93) and were sublimed before use. Ethyl vinyl ether was refluxed under nitrogen and over sodium for two hours, then distilled through a 20 cm Vigreux column. 1,1'-Azoisobutane was prepared by the method of Blackham and Eatough (94). 9,10-Diphenylanthracene (Aldrich) was recrystallized from

benzene and dried under vacuum. Benzene, n-hexane, cyclohexane (Fisher spectroanalyzed) and acetonitrile (Matheson Coleman and Bell spectroquality) were used without further purification.

6.3 Preparation of Adducts

6.3.1 Irradiation of Adamantanethione and 2-Adamantylthiol

A benzene solution (30 ml) of adamantanethione (55.3 mg, 0.33 m mole) and 2-adamantylthiol (560 mg, 3.3 m mole) in a Pyrex irradiation tube was degassed then the tube sealed. The solution was then irradiated at room temperature using a Hanovia 450 watt medium pressure mercury lamp with a Corning 3-72 glass filter (λ>420 nm) until the orange-red color of adamantanethione had completely disappeared (2 hr.). The solution, on removal of benzene, gave a residue which was sublimed (70°C/0.5 mm Hg) to remove excess 2-adamantylthiol. The residue thus obtained was purified on tlc (Kieselgel DF-5) using petroleum ether (30-60°C) as eluent to give the disulfide 45 as colourless crystals (102 mg, 0.30 m mole, yield 92%). The analytical sample of this major product had m.p. 282-3°C after two recrystallization from absolute ethanol.

Analysis:

Calcd. for $C_{20}H_{30}S_2$	:	C, 71.82; H, 9.04; S, 19.14
Found	:	C, 72.17; H, 8.73; S, 19.01
Nmr spectrum (CCl_4)	:	3.12 (2H, broad singlet -CH-S-), 1.27 - 2.36 (28H, the balance of the protons).
Uv (n-hexane)	:	λmax. 252 nm (log ε 2.58).
Mass spectrum	:	334, 167, and 135.

6.3.2 Preparation of 2-Adamantyldisulfide

A solution of ferric chloride (135 mg, 0.83 m mole) in ethanol (1 ml) was added dropwise to a stirred solution of 2-adamantylthiol (100 mg, 0.59 m mole) in ethanol (15 ml). One drop of concentrated hydrochloric acid was added to the mixture. The disulfide precipitated and was isolated by filtration then recrystallized from absolute ethanol (84 mg, 0.25 m mole, yield 84). Its uv and nmr spectra and tlc behavior were identical with those of 2-adamantyldisulfide obtained from the irradiation of adamantanethione and 2-adamantylthiol, and gave no melting point depression on mixing with the latter sample.

6.3.3 Irradiation of Adamantanethione and 2-Deuterio-2'-Adamantylthiol

A mixture of adamantanethione (250 mg, 1.50 m mole) and 2-deuterio-2'-adamantylthiol (1 g, 5.9 m mole) (95) (93.48% d; the thiol was oxidized to the disulfide (see above) and the latter analyzed by mass spectrometry for deuterium content) was placed in a degassing bulb to which was joined a pyrex tube and a square quartz cuvet (1 cm) (see Figure 23) and degassed in the solid phase (5×10^{-5} mm Hg). Benzene (20 ml) was degassed (3 freeze-thaw cycles, 5×10^{-5} mm Hg) and distilled in the dark on to the solid mixture. The solution was then transferred from the degassing bulb (A in Figure 23) to the pyrex tube B and the sample cell was sealed at D.

The solution was then irradiated at room temperature using a Hanovia 450 watt medium pressure mercury lamp through a Corning 3-72 glass filter (λ>420 nm) for 10 min.. The disappearance of

2 2

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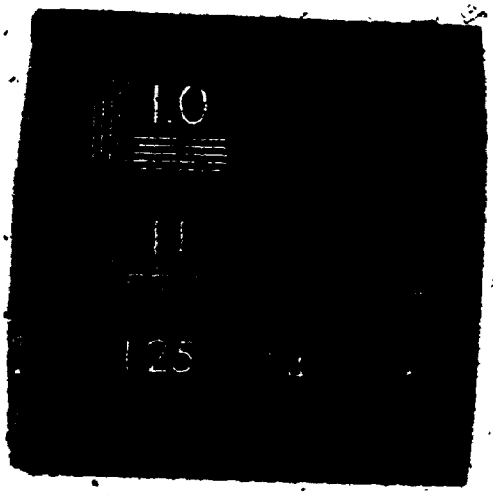

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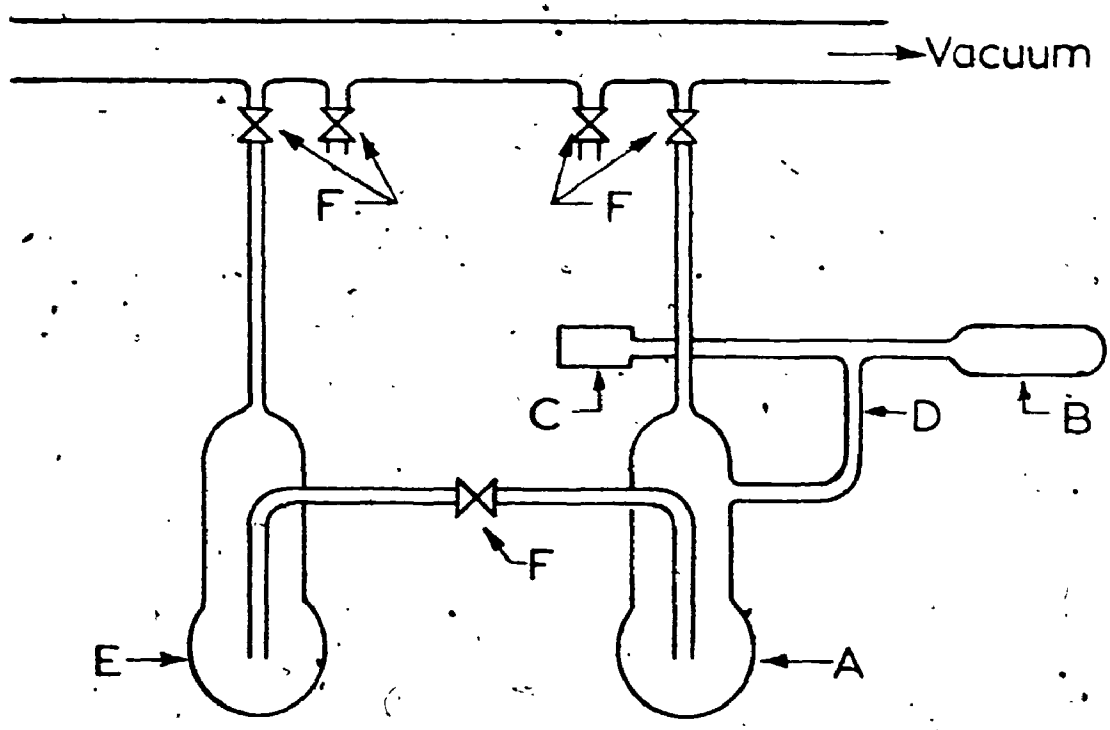

Figure 23. The Sample Cell for Degassing and Irradiation of Adamantanethione-2-Adamantylthiol.

A : degassing bulb where the solid mixture is put
B : pyrex tube, or 5 cm quartz cell with 28 mm O.D.
C : 1 cm square cuvet
D : joint
E : degassing bulb where benzene is put
F : greasless stopcoks.

adamantanethione was followed by monitoring its absorption at 500 nm using a Gilford 240 single beam spectrometer. Irradiation was continued until 8.36% of the starting thioketone was consumed.

After irradiation, the benzene solution was extracted four times with 50 ml portions of aqueous silver nitrate solution (2 g in 200 ml). The excess thiol precipitated as the silver mercaptide and was removed by centrifugation. The benzene layer was then washed with distilled water and dried over anhydrous magnesium sulfate. The solvent was then removed on a rotatory evaporator and the resultant residue was chromatographed on preparative tlc plates using petroleum ether (30-60°C) as eluent (a blank experiment established that no oxidation of 2-adamantylthiol to 2-adamantyldisulfide takes place). The zone which was visible under uv light, (RF 0.81) gave the disulfide 50 which was recrystallized from benzene-acetonitrile (1:2) and then analyzed by mass spectrometry for deuterium content. The observed relative peak intensities at m/e 334, 335 and 336 are given in Table 9 along with the calculated contributions to these peaks arising from the naturally occurring isotopes.

Table 9. Mass Spectrum of 50.

m/e	Observed Peak Intensity	Calcd. Contribution from Naturally Occurring Isotopes
334 (0-d)	5.00	0.00
335 (1-d)	100.00	1.20
336 (2-d)	26.48	24.45

6.3.4 Short Wavelength Irradiation of Adamantanethione and Ethyl Vinyl Ether

A n hexane solution (10 ml) of adamantanethione (166 mg, 1 m mole) and ethyl vinyl ether (1.9 g, 26.4 m mole) was degassed in a quartz irradiation tube which was then sealed. The solution was irradiated at 253.7 nm using a Rayonet reactor for 40 min. (50% conversion of the thioketone by uv analysis) and the solvent and excess ethyl vinyl ether then removed on a rotatory evaporator. Glpc analysis (6' x ¼", 10% Carbowax on chromosorb W column at 185°C) of the residue showed that it contains at least ten peaks. Chromatography on preparative tlc plates (Kieselgel DF-5; petroleum ether 30-60°C-methylene chloride 1:1 eluent) gave three broad zones. The upper zone was not investigated, the middle zone contains the thioketone and the lower zone was extracted with chloroform and the fraction obtained was further separated into two components (ratio 2:1) using glpc (6' x ¼", 10% carbowax on chromosorb W, column at 185°C). The minor component was shown to be identical to an authentic sample of the thietane 17 prepared by Liao (31) by V.P.C. retention time and by ir and nmr spectroscopy. The major component (thietane 29) was further purified by tlc (Kieselgel DF-5; petroleum ether 30-60°C-methylene chloride 1:1 eluent) and an analytical sample prepared by distillation of the solvent free sample at 90°C/0.03 mm Hg.

Precise mass determination

Calcd. for $C_{14}H_{22}SO$	:	238.1386
Found	:	238.1356
Nmr spectrum (CCl_4)	:	See Table 4 and Figure 11.

Mass spectrum : 238, 166 and 148.

6.3.5 Short Wavelength Irradiation of Adamantanethione and Cyclohexane

A cyclohexane solution (10 ml) of adamantanethione (166 mg, 1 m mole) was degassed in a quartz irradiation tube which was then sealed. The solution was irradiated at 253.7 nm using a Rayonet reactor for 50 min. (70% conversion of the thioketone by uv analysis) and the solvent then removed on a rotatory evaporator. Glpc analysis (6' x ¼", 10% SE-30 on chromosorb P column at 190°C) of the residue showed that it contains two major peaks in a ratio of ~2:1. Preparative glpc separation was carried out. The major component, 2-cyclohexylthioadamantane was further purified by tlc (Kieselgel DF-5; petroleum ether 30-60°C) and the solvent free sample distilled at 70°C/0.04 mm Hg.

Mass spectrum : 250, 166 and 135.

Nmr spectrum (CCl_4) : 2.98 (1H, broad singlet -CH-S-C_6H_{11}), 1.1 - 2.6 (25H, the balance of the protons).

Similarly, the minor component (the thiol 32) was further purified by tlc and distilled at 70°C/0.04 mm Hg.

Mass spectrum : 250, 216 (parent peak), 167, 166, and 135.

Nmr spectrum : 1.2 (sharp singlet -SH), 1.0 - 2.7 (25H, the balance of the protons).

6.3.6 Preparation of 2-Cyclohexylthioadamantane

An acetone solution (20 ml) of 2-adamantylthiol (500 mg, 2.9 m.mole) and cyclohexene (400 mg, 4.8 m.mole) was degassed in a pyrex tube. The solution was then irradiated using a Hanovia 450 watt medium pressure mercury lamp with a pyrex jacket for 30 min.. A white substance precipitated out. The solution was filtered and the acetone and excess cyclohexene then removed on a rotatory evaporater. 2-Cyclohexylthioadamantane was collected using preparative glpc separation (6' x ¼", 10% SE-30 on chromosorb P at 190°C), further purified by tlc and distilled as described in section 6.3.5. Its nmr and mass spectra, tlc and glpc behavior were identical with those of 2-cyclohexylthioadamantane obtained from the irradiation of adamantanethione in cyclohexene at 253.7 nm.

6.4 Quantum Yields

6.4.1 Adamantanethione-2-Adamantylthiol System

Apparatus

The optical bench system used has been described previously (96). The source was a Compact arc 150 watt Xenon Hanovia lamp. The lamp was housed in a brass case and part of its light was gathered by a planar-convex lens in the front of the box, and directed through a series of lenses to collimate it to a diameter of about 15 mm. The light beam was then passed into the sample holder (a light tight box) where it was split by a quartz beam splitter; of the incident light about 92% was transmitted while the balance was reflected at 90° to the incident beam. Semicircular brass cradles were disposed in the path of both the reflected and transmitted beam to accommodate the

cylindrical sample cells. 468 nm Irradiation light was obtained employing a combination of a Bausch and Lomb monochromator grating (1200 grooves/mm) and a Corning filter C.S. 0-52. The solutions were irradiated in quartz cells (5 cm x 28 mm O.D) which were attached to the degassing bulb (see Figure 23) by a greaded seal.

Procedure

The amount of light absorbed by the sample was measured using the 0.15 M potassium ferrioxalate actinometer developed by Parker (97).

The samples were prepared and degassed in the same manner as for the irradiation of adamantanethione-2-deuterio-2'-adamantylthiol system described in section 6.3.3.

Irradiations were carried out to between 10 and 13% conversion of adamantanethione. The disappearance of adamantanethione was followed by monitoring its absorption at 500 nm using a Gilford 240 single beam spectrometer. The quantum yield of adamantanethione disappearance which was taken to be equal to that of disulfide formation was calculated using the following equation [45]

$$\Phi = \frac{\text{wt. of thione/consumed/M.W. of thione}}{A}$$

A is the number of photons absorbed (from actinometry determination).

6.4.2 Quantum Yields of Dimer Formation at 250 nm

Apparatus

The quantum yields of dimerization were determined on a Jasco Model CRM-FA spectroirradiator. The entrance slitwidth was 2 mm and the reference wavelength was 620 nm.

Procedure

A model 105 Integrator was used to measure radiation dosage at about 850 nm. The count number of the integrating counter was proportional to the total radiation dosage. The counter (range x1) was calibrated by ferrioxalate actinometry (97). A solution (3.4 ml) of potassium ferrioxalate (0.006 M) in sulfuric acid (0.1N) was pipetted in the dark into a quartz square (1 cm) cuvet. The cuvet was put in the eighteenth sample cell holder of the spectroirradiator (250 nm at the centre, half band width = 3.75 nm). A slit (5 x 20 mm) was placed in front of it. Irradiation was carried out until the integrating counter (range x1) read "75". The sample was then stirred thoroughly and a 1 ml aliquot pipetted into a 25 ml volumetric flask containing 2 ml of 1,10-phenanthroline solution (0.1%) and 0.5 ml of buffer solution (0.6N sodium acetate and 0.36N sulfuric acid). The resulting mixture was diluted with distilled water to a total volume of 25 ml and the solution then allowed to stand for at least half an hour. The optical density at 510 nm in a 1 cm cell was measured using a Gilford spectrophotometer 240, and the measurement converted to the concentration of ferrous ion using a calibration graph (previously obtained from known concentrations of ferrous ion). The irradiation dose was calculated from the quantity of ferrous ion in the total volume of the irradiated solution using the quantum yield as 1.25.

The sample cell for irradiation was constructed by joining a square quartz cuvet (1 cm) to a degassing bulb made from a pyrex tube as shown in Figure 24.

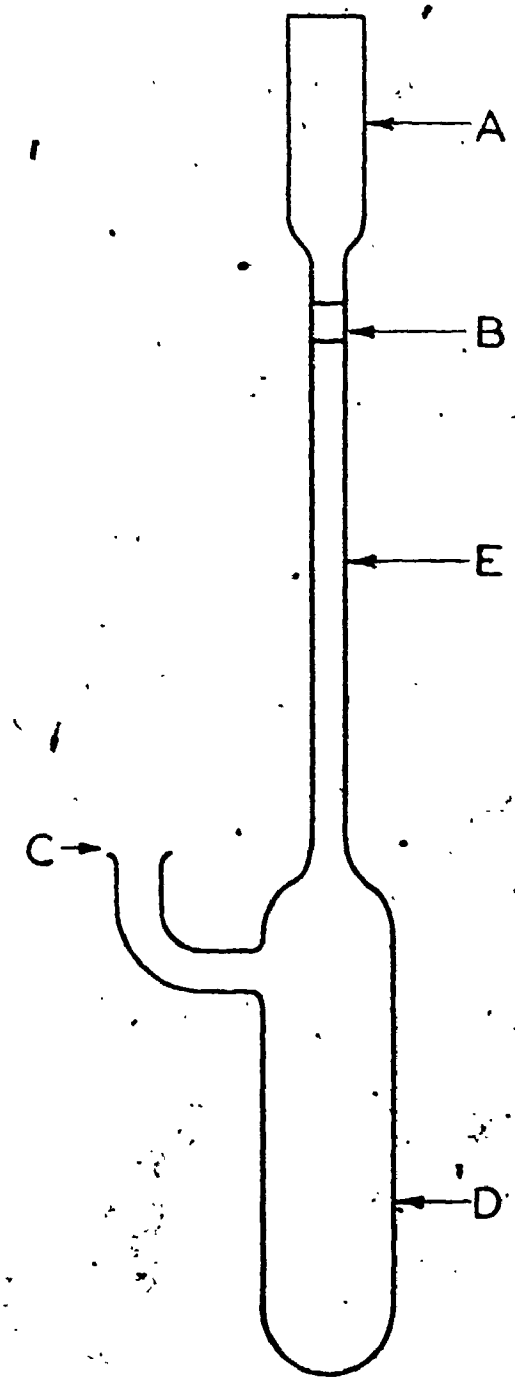

Figure 24. The Sample Cell for Quantum Yield Determination.

A : 1 cm square quartz cuvet
B : joint
C : To vacuum
D : Degassing bulb (pyrex)

A solution of adamantanethione in n-hexane (4 ml; various concentrations) was pipetted into the degassing bulb. After degassing, the solution was transferred from the degassing bulb to the quartz cuvet and the sample was sealed (at E in Figure 24).

Irradiations were carried out to between 1 and 2% formation of dimer. The analysis for the dimer was carried out on a Varian Aerograph Hy-Fi 600-C gas chromatograph equipped with a flame ionization detector. The column used was 2½' x 1/8" 3% Poly-A-103 operating at 230°C. 9,10-Diphenylanthracene was used as an internal calibrant.

The quantum yields of dimer formation at 278 ± 3.75 nm and 500 ± 7.5 nm were measured by the same procedure described above with the following exception: since the quantum yield of dimer formation at 500 nm was very low, a 10 mm slit was used in front of the sample cell. In all dimerization experiments a blank solution was kept in the dark (the cell was wrapped in aluminum foil) during the period of irradiation and the dimer was analyzed as above and the correction made.

The relative intensities (in terms of energy) of incident light at 278 nm and 500 nm were determined by a Model RMD-1 (DC type) radiometer using a thermopile as a detector.

6.4.3 Quantum Yields of Thietane 17 Formation

The quantum yields of thietane 17 formation at 500 ± 7.5 nm and 250 ± 7.5 nm were measured in the manner described by Liao (31) with the following changes: at 500 nm, fluoranthene was used as the calibrating compound and the thietane was analyzed on a Varian

Hy-Fi 600-C gas chromatograph using a 6' x 1/8", 3% SE-30 on chromosorb P column operating at 190°C, and at 250 nm, 2-cyclohexylthioadamantane was used as the calibrating compound and the thietane analyzed on a Varian Aerograph series 1700 gas chromatograph, using a 6' x ¼", 10% carbowax on chromosorb W column operating at 185°C.

6.4.4 Quantum Yields of Sensitized Reactions

Sensitization of Dimer Formation

A solution (4 ml) of Michler's ketone (0.01 M), and adamantanethione (0.2 M) in benzene was degassed and irradiated (λ = 362 ± 7.5 nm) in the same manner as that described in section 6.4.2 and the same procedure was followed for the analysis of dimer formation.

Sensitization of Thietane 17 Formation

A solution (4 ml) of triphenylene (0.01 M), adamantanethione (0.2 M) and ethyl vinyl ether (2 M) in benzene was degassed and irradiated (λ = 306 ± 7.5 nm) in the same manner as that described previously in section 6.4.3. After irradiation, glpc analysis of the thietane formed was carried out in the same way as that described for thietane formation at 500 nm.

6.4.5 Quenching of Dimer Formation at 250 nm with 1,1'-Azoisobutane

Samples (4 ml) of solutions of adamantanethione (6.46×10^{-3} M) and 1,1'-azoisobutane (various concentrations 0-0.199 M) in n-hexane were degassed and irradiated in a manner identical to that described in section 6.4.2. The irradiated solutions

were analyzed by the previously described glpc method (section 6.4.2). A plot of Φ_0/Φ against the concentration of 1,1'-azoisobutane was then made (see Figure 12).

6.4.6 Quenching of Thietane 17 Formation at 250 nm with 1,1'-Azoisobutane

Samples (4 ml) of solutions of adamantanethione (0.1 M), ethyl vinyl ether (1.0 M) and 1,1'-azoisobutane (various concentrations 0-0.45 M) in n-hexane were degassed, irradiated and analyzed in a manner identical to that described in section 6.4.3.

6.5 The Disappearance of Adamantanethione at 253.7 nm as a Function of the Solvent

Solutions (4 ml) of adamantanethione (0.048 M) in cyclohexane and acetonitrile were degassed and irradiated at 253.7 nm using a Rayonet reactor. The disappearance of the thione was followed by monitoring its n,π^* absorption (see Figures 16 and 17).

6.6 Determination of Relative Yield of Thietanes 29 and 17

6.6.1 Relative Yield of Thietanes 29 and 17 as a Function of Percentage Conversion

Solutions (4 ml) of adamantanethione (0.1 M) and ethyl vinyl ether (2.0 M) in cyclohexane were degassed and irradiated at 253.7 nm using a Rayonet reactor to different percentages of conversion. The disappearance of the thione was followed by monitoring the absorption at 500 nm using a Gilford 240 spectrometer. The thietanes were analyzed on a Varian Aerograph series 1700 gas chromatograph using a

6' x ¼", 10 carbowax on chromosorb W column at 185°C. The ratio of thietanes 29 to 17 was measured by integrating the area under the peaks using a planimeter.

6.6.2 Relative Yields of Thietanes 29 and 17 as a function of the Solvent

The procedure was the same as mentioned above. The solvents used were cyclohexane and acetonitrile. The samples were irradiated to about 17 conversion.

6.7 Laser Flash Photolysis

The flash photolysis apparatus has been previously described by Bonneau (43). Quadrupled (265 nm) and doubled (530 nm) neodymium laser emissions were used as wavelengths of excitation.

6.7.1 Adamantanethione Triplet

A solution of adamantanethione in n-hexane (1.3×10^{-3} M) was degassed in a degassing bulb to which was attached a square quartz cuvet (1 cm). The solution was then transferred from the degassing bulb to the quartz cell and flashed at 265 nm. The transient absorption was monitored at 280 nm and the oscilloscope trace was photographed.

Kinetic Analysis of Decay Curves

An enlargement of the oscilloscope trace representing the decay of absorbence of the transient is shown in Figure 25. "d" Is the trace of the decaying transient absorbance, I_o is the intensity of incident light and I is the intensity of transmitted light. Beer's law was assumed for the transient absorption,

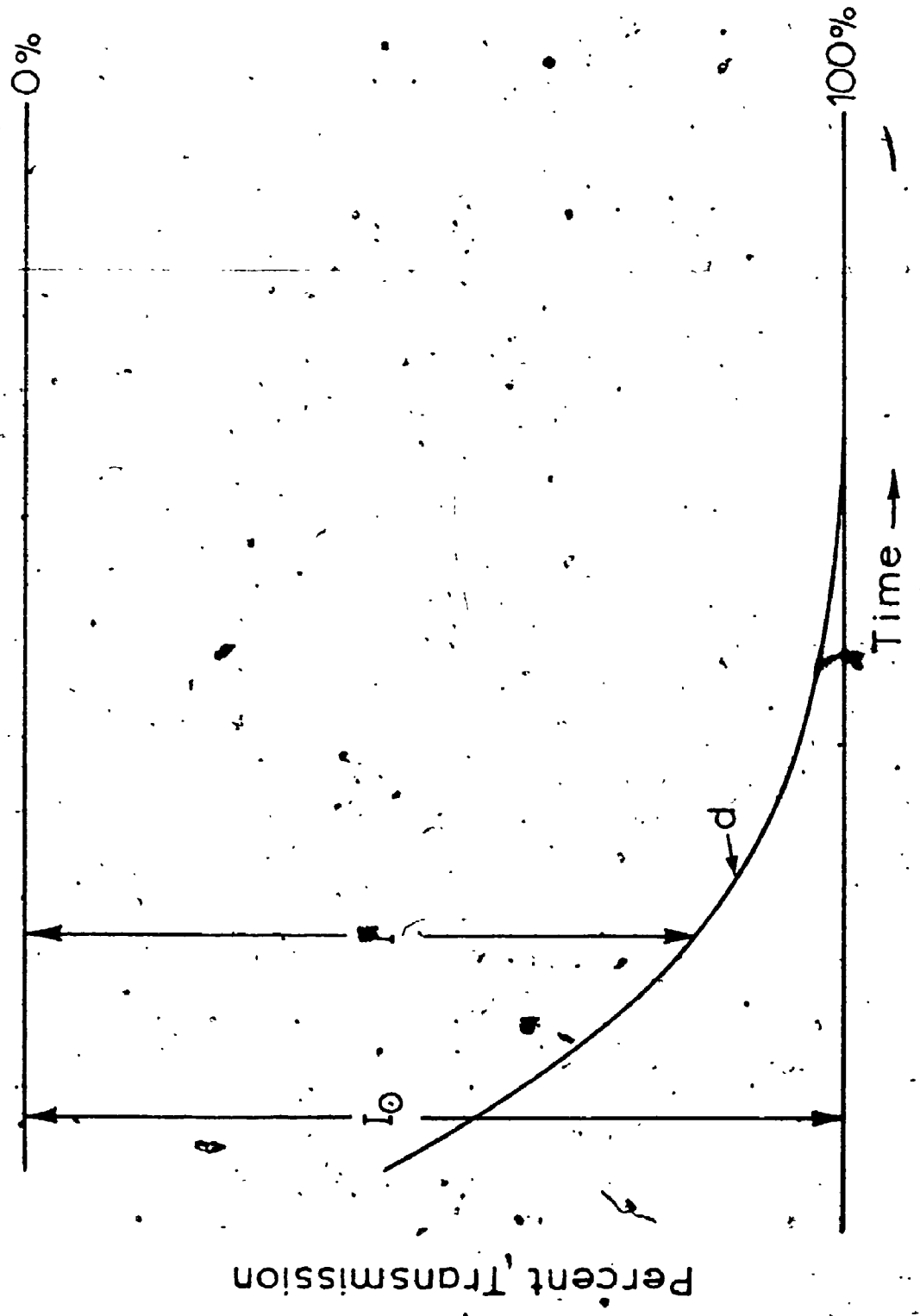

Figure 25. The Decay of Absorbence of the Transient.

$$\log I_0/I = \varepsilon cl$$

where ε is the molar extinction coefficient, c is the concentration of the absorbing species in moles/litre and l is the path length in cm. A first order plot (log log I_0/I versus the time) was made (see Figure 26), and the unimolecular rate constant for decay was calculated from the slope.

6.7.2 The Triplet Absorption Spectrum of Adamantanethione

A part of the spectrum of adamantanethione triplet was obtained by flashing a degassed solution of the thione (1.97×10^{-3} M) in n-hexane at 530 nm (path length 5 cm). The relative transient absorption at 280, 290, 300, 310 and 330 nm was recorded and plotted versus the wavelength (see Figure 2).

6.7.3 Effect of Concentration on the Triplet Lifetime of Adamantanethione

Samples of solutions of adamantanethione (various concentrations, 1.9×10^{-4} - 5.05×10^{-3} M) in n-hexane were degassed and flashed at 265 or 530 nm; the transient absorption was monitored at 280 nm, and the rate constants for decay were calculated from the first order plot. The results are shown in Table 1 and Figure 3.

6.7.4 Quenching of the Transient at 530 nm with 1,1'-Azoisobutane

Samples of solutions of adamantanethione (5×10^{-4} M), and 1,1'-azoisobutane (various concentrations, 0-0.04 M) in n-hexane were degassed and flashed at 530 nm (path length 5 cm); the transient absorption was monitored at 280 nm and the rate constants for decay

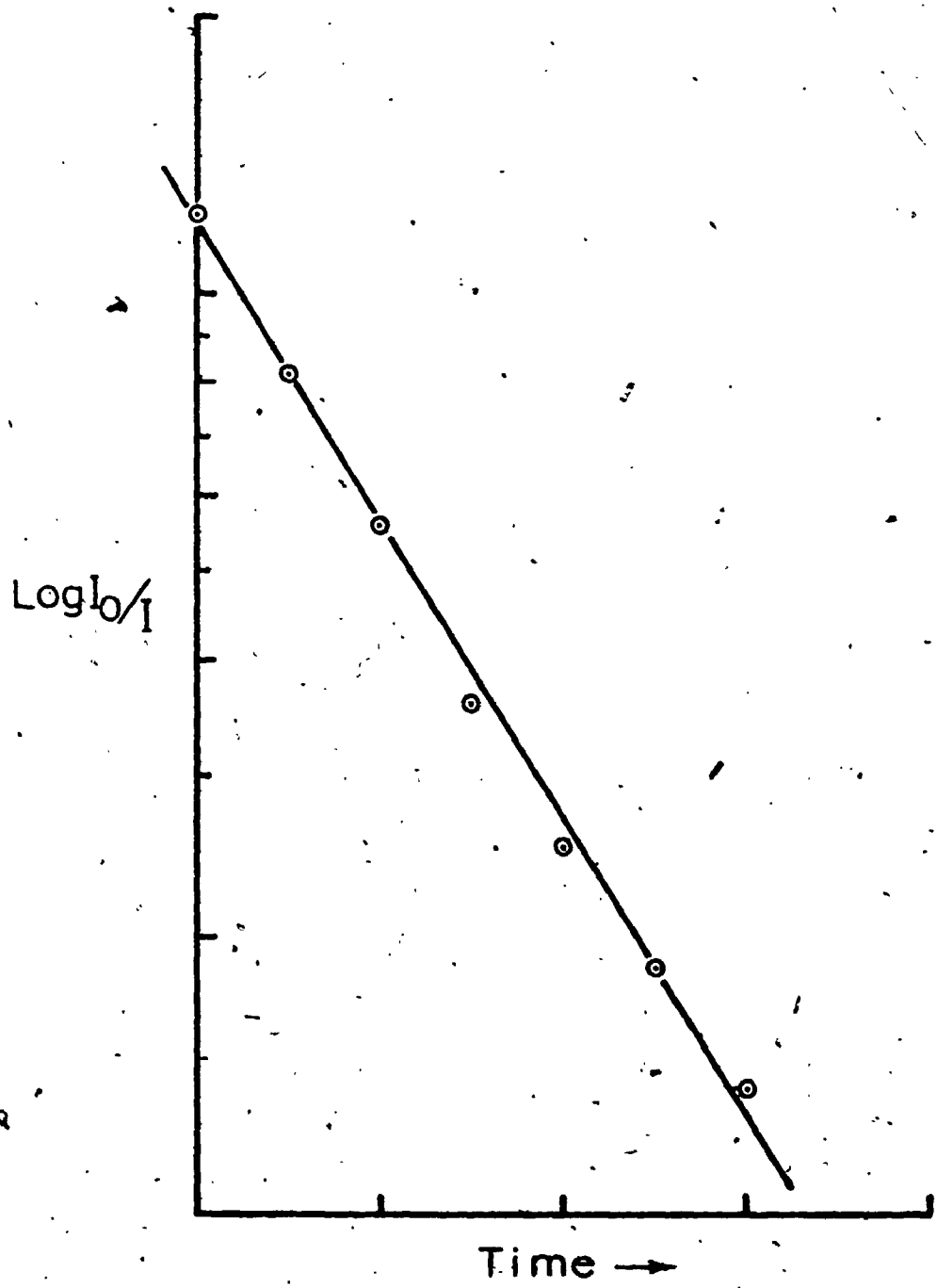

Figure 26. A First Order Plot (on Semi-Log Scale).

were calculated from the first order plot. A plot of τ^{-1} against the concentration of 1,1'-azoisobutane was made (see Table 2 and Figure 4).

6.7.5 Determination of Ratio of Transient Yields

A solution of adamantanethione (1.43×10^{-3} M) in n-hexane was degassed and flashed at 265 nm (path length 1 cm) and at 530 nm (path length 5 cm) and the transient absorption was monitored at 280 nm (see Table 10).

Table 10. Relative Intensity of Transient Absorption

λexcitation (nm)	I/I_o
265	0.164
265	0.164
530	0.580
530	0.540

The light intensity of 265 nm was measured using the iodide ion reaction studied by Jortner (98), and that at 530 nm using a microcalorimeter (1000 μv/J). Corrections for light intensity (number of photons per flash) and percentage absorption by the sample were applied.

At 265 nm: The number of photons per flash (from actinometry determination) was found to be 2.5×10^{16}. A solution of the thione (1.43×10^{-3} M; path length 1 cm) absorbs only 90% of the incident light. It follows that the number of photons absorbed by the sample per flash is 2.25×10^{16}.

At 530 nm: The number of photons per flash was found to be

1.166×10^{16}. The same solution of thione (1.43×10^{-3} M; path length 5 cm) absorbs only 6% of the incident light. The number of photons absorbed by the sample per flash is therefore 6.996×10^{16}.

The ratio of transient yields at the two wavelengths was calculated as follows

$$I/I_o \text{ (530 nm)} = 0.56$$

$$I/I_o \text{ (265 nm)} = 0.164 \times \frac{6.996 \times 10^{16}}{2.25 \times 10^{16}} = 0.508$$

$$\frac{I/I_o \text{ (265 nm)}}{I/I_o \text{ (530 nm)}} = 0.907$$

6.8 Luminescence

6.8.1 Emission Spectra of Adamantanethione

The emission spectra of adamantanethione were obtained in E.P.A. (Aminco: Ether, iso-pentane, alcohol, 5:5:2) or Methylcyclohexane-n-pentane (4:1 mixture) at 77°K following the same procedure described by Blackwell et al (42).

6.8.2 Fluorescence and Phosphorescence Quenching of Triphenylene

The apparatus has been previously described by Loutfy (84).

Two solutions of triphenylene (4 ml; 0.001 M), one containing adamantanethione (0.05 M), were made up in methylcyclohexane-n-pentane (4:1 mixture) and degassed in pyrex bulbs attached to tubes of Suprasil quartz. After degassing, the solutions were transferred to the quartz tubes and irradiated at 330 nm (the light source was a 150 watt xenon Hanovia lamp, the output of which was passed through a

Bausch and Lomb 0.25-m monochromator). A Corning glass filter 0-52 was placed in front of the entrance slit of the monochromator to prevent scattered light. The fluorescence spectra were recorded at room temperature (see Figure 9).

The two tubes containing the previously described solutions were consecutively placed in a liquid nitrogen cooled quartz dewar which had a 10 mm glass ring at the top and a polyethylene plug at the bottom so that the positioning of the tubes was reproducible. Excitation was conducted at 330 nm and the phosphorescence of triphenylene recorded (see Figure 10).

6.8.3 Stern-Volmer Plot; Quenching of Fluorescence of Triphenylene with Adamantanethione

The apparatus used and the details of the technique have been described by Ware (99).

Samples (5 ml) of solutions of triphenylene (0.01 M) and adamantanethione (various concentrations 0-0.2 M) in benzene were degassed with a stream of nitrogen for 15 min., stoppered and irradiated at 313 nm. The fluorescence observed through the back of the cell was monitored at 365 nm. The results are shown in Table 3 and Figure 8.

The fluorescence lifetime of triphenylene at 0.01 M concentration was measured with the single photon time correlation technique by Dr. C. Lewis.

6.8.4 Detection of Upper Limit of Fluorescence from Adamantanethione

Apparatus

The light source was a monochromatic beam (530.9 nm) from a Spectra-Physics Krypton Laser Model 164-01. The beam was reflected by a mirror (angle of incidence 45°) through the sample and the emission viewed at right angle to the irradiating light. The fluorescence was monitored at 600 nm using a Heath monochromator (slit width 2 mm) equipped with a EMI 9558QD photomultiplier (S-20 response) which was cooled with solid carbon dioxide. This was connected to a Hewlett & Packard DC micro volt ammeter Model 425AR.

Procedure

A rhodamine B solution in alcohol (O.D at 530.9 nm = 0.72, path length 1 cm) was diluted successively by one tenth and the output of the photomultiplier noted for each solution. After five dilutions (O.D = 7.2×10^{-6}), no deflection was registered on the micro volt ammeter. For a solution of adamantanethione in n-hexane (O.D at 530.9 nm = 2×10^{-2}, path length 1 cm), no fluorescence was detected. Taking ϕ_{fl} for rhodamine B equal to unity (64), the upper limit for the quantum yield of fluorescence ϕ_A from adamantanethione was calculated using the following equation.

$$\phi_A = \frac{\phi_R \times O.D_R}{O.D_A}$$

where ϕ_R = the quantum yield of fluorescence of rhodamine B.

$O.D_R$ = Optical density of rhodamine B solution.

$O.D_A$ = Optical density of adamantanethione solution.

6.9 Investigation of Validity of Beer's Law

6.9.1 Wavelength Effect

Samples (5 ml) of solutions of adamantanethione (various concentrations) in n-hexane were prepared and the optical density measured at 263.5, 275 and 465 nm using a Gilford Model 240 spectrometer (see Table 7 and Figures 14 and 15).

6.9.2 Solvent Effect

The same procedure described above was followed and the results for n-hexane and acetonitrile are shown in Table 7 and Figure 14.

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